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Effect of diluents on the extraction and separation of Fe(III) and Cu(II) from hydrochloric acid solutions using *N,N,N′,N′*-tetrabutyl succinamide

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ABSTRACT

The performance of extraction and stripping of Fe(III) using *N,N,N′,N′*-tetrabutyl succinamide (TBSA) in different diluents from hydrochloric acid solutions was investigated. The effects of hydrochloric acid concentration, extractant concentration and temperature on the extraction of Fe(III) were studied. The extraction ability of TBSA in different diluents follows the order: kerosene/octanol($v:v = 7:3$) < cyclohexane < toluene. The extraction distribution ratio increases with an increase in hydrochloric acid concentration and extractant concentration. The extraction reaction is exothermic and the extraction distribution ratio of Fe(III) with TBSA decreases gradually with increasing temperature. The composition of the Fe(III) extracted species was obtained. The partition of Cu(II) was also investigated and the separation factor of Fe(III) relative to Cu(II) is nearly 140 under the studied conditions, which indicates that TBSA is a good extractant for the separation of Fe(III) from $CuCl_2$ liquor in copper hydrometallurgy.

1. Introduction

Much attention has been given to the purification of minerals and recovery of leached residues due to the scarcity of high grade ore. Chloride hydrometallurgy plays a significant role in refining minerals in current industrial processing because it avoids the release of SO_2 which is generated in traditional smelting processes (Cai et al., 2012). Solvent extraction has been widely used in metal separation and enrichment (Chen, 2004; Kyuchoukov and Mihaylov, 1991; Ye et al., 2000). Solvent extraction of Fe(III) has an important role in hydrometallurgy, wastewater treatment, environmental monitoring and analysis of soil (Mishra et al., 2011). Mishra et al. reported a comparative study on the extraction of Fe(III) from HCl leach liquors produced from the processing of low grade iron ore tailings using tri-n-butyl phosphate (TBP) with Cyanex 921 and Cyanex 923 in distilled kerosene (Mishra et al., 2010). Sinha et al. (2014) reported liquid–liquid extraction and separation of zinc and iron values from a spent pickle solution and Co-extraction of Zn(II), HCl and Fe(III) was noticed with the extractants (amine/amine + HDEHP) without any appreciable selectivity. Fe(II) was not extracted by the solvent and Zn(II) was extracted selectively leaving Fe(II) in the raffinate.

Copper chloride hydrometallurgy is an active research area, not only due to higher copper leaching kinetics and recovery, but also because of environmental concerns when compared to smelting and leaching of other media such as sulfuric acid (Lu and Dreisinger, 2013). However, the leach liquors of copper ores always contain other metal ions, such as iron (Al-Harahsheh et al., 2008). Therefore, the separation of Cu and Fe ions is of importance in view of recovery of high purity. Unfortunately, it was found that the commercially available aromatic hydroxyoxime extractants for extraction of copper from sulfate solutions, such as LIX984N, CLX50 and LIX54 were not suitable for the extraction of copper from chloride solutions, due to their low extraction capacity and small separation factors of copper over iron (Zhu et al., 2012). Even though Rabah (2000) has reported an extraction method to recover copper and deposition method to recover iron separately from spent hydrochloric acid used to clean dirty car radiators by using LIX 860, it is still particularly important to find a good extractant that can separate iron from copper in chloride solution efficiently.

Over the last decade, amide extractants have been developed rapidly (Sun et al., 2008; Zhang et al., 2001). Unlike the organophosphorus extractants which produce P_2O_5 and H_3PO_4 by incineration, the incinerated amides produce only gases which can be easily separated from non-incinerable contaminants, so there are no secondary waste products (Thiollet and Musikas, 1989). Alkyl malonamides can efficiently and selectively remove Fe(III) from concentrated chloride solutions (Paiva and Costa, 2005; Santos and Paiva, 2014). A solvent extraction method using N,N-diethyldodecanamide (DEDOA) to remove Fe(III) from a synthetic nickel chloride leach solution was investigated. Using an organic system consisting of 30% (v/v) DEDOA and 30% (v/v) isodecanol (as phase modifier), over 90% Fe(III) was extracted from the strong chloride solution (6 M Cl^-) in a single contact and high selectivity of Fe(III) over other metals was obtained (Zhu et al., 2014).

In this paper, the extraction of Fe(III) and Cu(II) from hydrochloric acid solutions using *N,N,N′,N′*-tetrabutyl succinamide (TBSA) as the extraction agent in different diluents was investigated.

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2. Materials and methods

2.1. Materials

All the chemicals and reagents used in this study were of analytical grade. *N,N,N′,N′*-tetrabutyl succinamide (TBSA) (purity > 98%) was synthesized by the reaction of succinyl dichloride and di-n-butylamine in dichloromethane and triethylamine as an acid scavenger (Mowafy and Aly, 2001). The final products were characterized by elemental analysis, IR and ^{1}H NMR and the purity was higher than 98%. The structure of TBSA is shown in Fig. 1. Fe(III) solutions were prepared by dissolving $FeCl_3 \cdot 6H_2O$ in hydrochloric acid solutions, and diluting to 0.005 M. Kerosene/octanol, cyclohexane and toluene were used as the diluents in the present study. The extraction organic phase was thus obtained by dissolving TBSA in these diluents, respectively. The concentration of TBSA was 0.1 M unless otherwise specified.

2.2. Extraction experiments

Initial experiments on the effect of time on the distribution of metal ions in the two phases showed that 30 min is sufficient to reach equilibrium. Equal volumes of the aqueous and organic phases were shaken for 30 min at a constant temperature. The concentration of Fe(III) in the aqueous solution was determined by visible spectrophotometry using 1,10-phenanthroline as the chromogenic reagent (Huang et al., 2008). As no precipitate or third phase formation was observed, it was assumed that no Fe(III) mass loss occurred during the extraction and stripping experiments. Therefore, the iron concentrations in the organic phases were calculated by mass balance (Ribeiro et al., 2013). The distribution ratio, D, is taken as the ratio of the concentration of the metal ion in the organic phase to that in the aqueous phase after extraction. Pure water was used to strip Fe(III) from the organic phase. The volume ratio of water to the organic phase was 1:1 and the stripping procedure was carried out at 298 K for 30 min.

Cu(II) solution was prepared by dissolving $CuCl_2 \cdot 2H_2O$ in hydrochloric acid solution and then diluting to produce 0.0025 M Cu at different acid concentrations. The extraction method for Cu(II) was similar to that for Fe(III) and the concentration of Cu(II) in the aqueous phase after extraction was measured by visible spectrophotometry using cuprizon as the chromogenic reagent (Qi et al., 2011).

The extraction of HCl from HCl solutions without Fe(III) was conducted under the same conditions as that for Fe(III). The concentration of hydrogen ions in the aqueous phase was measured by acid–base titration against standard Na_2CO_3 which had been dried at 300 °C for 2 h. The concentration of H^+ in the organic phase was obtained by acid–base titration against standard Na_2CO_3 dissolved in ethanol/water (V/V = 1:1).

2.3. IR spectra of loaded organic phases

IR spectra were recorded with a liquid cell using a Perkin-Elmer SPECTRUM ONE spectrophotometer in the range of 4000–400 cm^{-1}. Extraction experiments were carried out with a $C_{TBSA} = 0.50$ M (with different diluents), $C_{Fe^{3+}} = 0.10$ M and $C_{HCl} = 4.74$ M. Then organic phases were separated and diluted to a certain concentration to be tested by IR spectroscopy. NaBr optical cell was washed before use with the solvent to be investigated. The cell was filled with the liquid sample and placed in the IR instrument using pure diluent as the blank.

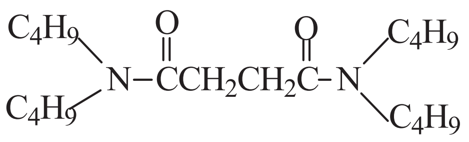

Fig. 1. Structure of TBSA.

3. Results and discussion

3.1. Effect of HCl concentration on the extraction of Fe(III)

The effect of hydrochloric acid concentration on the extraction of Fe(III) in different diluents was investigated. Fig. 2 illustrates that the distribution ratio of Fe(III) increases with the hydrochloric acid concentration, which can be attributed to the formation of $[FeCl_4^-]$. The extraction distribution ratio of Fe(III) is very low with hydrochloric acid concentrations less than 2.85 M. The extraction distribution of Fe(III) increases sharply at hydrochloric acid concentrations above 2.85 M. The results also indicated that the extraction distribution ratio of Fe(III) in various diluents under the same conditions increases in the order: kerosene/octanol(v:v = 7:3) < cyclohexane < toluene.

3.2. Effect of extractant concentration on the extraction of Fe(III)

UV–visible spectra were recorded to establish the structure of the extracted species in the organic phase when toluene was used as diluent (Fig. 3). There are strong absorption peaks at 364 nm and 314 nm, which are both characteristic absorption peaks of $[FeCl_4]^-$ (Biswas and Begum, 1999; Lever, 1968; Metzler and Myers, 1950). H^+ concentration in the organic phase was equal to the concentration of Fe(III) in the organic phase. This shows that the reaction has a solvation mechanism between $HFeCl_4$ and TBSA. These results further show that $HFeCl_4 \cdot nTBSA$ is the main product of the extraction process in the organic phase.

The results of the extraction of hydrochloric acid show that TBSA cannot extract HCl from a hydrochloric acid solution when iron is not present in the aqueous phase. This is different from the results of the extraction of nitric acid using diglycolamide, in which HNO_3 was extracted into organic phase and aggregation of extractant, H_2O and HNO_3 was found in the diluents (Nave et al., 2004; Panja et al., 2012). IR spectra of TBSA in toluene were checked and there was no change in the position of C═O peaks at different TBSA concentrations, which shows that there is no apparent aggregation of extractant in the organic phase under the studied conditions.

It is known that metal complexes of Fe(III) with Cl^- are formed in solution by a stepwise reaction as shown in Eqs. (1)–(4) (Bjerrum and Lukes, 1986). Navarro published the relationship of the percentage of each iron(III) chloride species in solution vs. the concentration of Cl^- (Navarro et al., 2009). The percentage of $FeCl_4^-$ increases with Cl^-

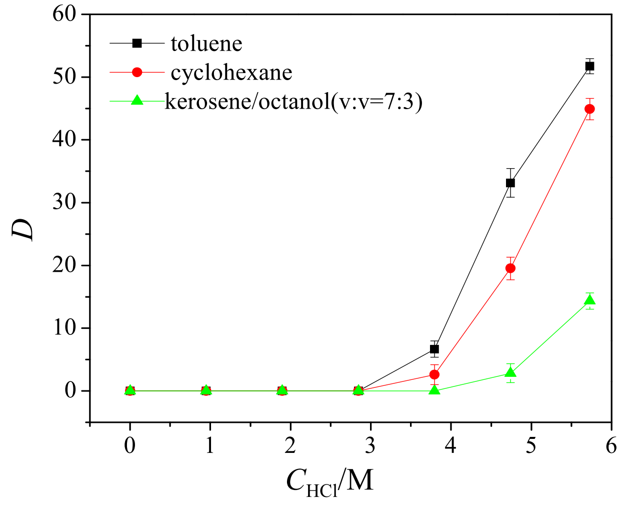

Fig. 2. Effect of HCl concentration on the extraction distribution ratio of Fe(III). $C_{Fe^{3+}} = 0.005$ M; $C_{TBSA} = 0.10$ M; and 298 K.