



# Zinc extraction from chloride solutions with mixtures of solvating and chelating reagents



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## ARTICLE INFO

### Article history:

Received 20 September 2015

Received in revised form 8 December 2015

Accepted 29 February 2016

Available online 2 March 2016

### Keywords:

Zinc

Solvent extraction

Pyridinecarboxamide

$\beta$ -Diketone

Extractant mixture

## ABSTRACT

An equimolar mixture of weakly basic and chelating reagent was used for extracting zinc(II) from acid chloride solutions at various concentrations of chloride and hydrogen ions. N,N-dihexylpyridine-3-carboxamide was used as a weak base and 1-phenyldecane-1,3-dione ( $\beta$ -diketone) as a chelating extractant. In a three-step extraction–scrubbing–stripping process, zinc ions were transferred from the chloride into the sulfate solutions. In the first step, Zn(II) was extracted by N,N-dihexylpyridine-3-carboxamide. The composition of the extracted complexes (solvate or ion pairs) depends on HCl concentration. After zinc(II) extraction from acid chloride solutions,  $\text{Cl}^-$  ions were scrubbed out from the organic phases with ammonia solutions. In this step, the extractants transfer zinc ions according to one of two possible mechanisms: from the solvate into the chelate, or from the ion pair into the chelate. The stripping of zinc ions from the chelate complex with  $\beta$ -diketone was carried out with sulfuric acid solutions. For both systems under investigation (weakly and strongly acidic solutions), the use of the reagent mixture enables the effective extraction of zinc(II) and removal of chloride ions from the organic phase. Owing to the possibility of using the extractant mixture for the recovery of Zn(II) from the chloride solutions of varied acidity, a partial protonation of the weakly basic extractant in the stripping step has no significant effect on the efficiency of a subsequent extraction–scrubbing–stripping process.

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## 1. Introduction

The hydrometallurgical processes in chloride media are particularly useful for zinc recovery from low-grade ores, complex sulfide ores, and also secondary zinc materials. In a number of processes, the extraction–stripping step is used for the purification and the concentration of zinc(II) chloride solutions. However, metal recovery from chloride solutions by electrowinning, which is the last step of a hydrometallurgical process, presents many difficulties. Metal formation in powder form instead of sheets and the recycling of chlorine gas are major problems, but they do not occur in sulfate electrowinning.

To avoid electrowinning from chloride media, the extraction–stripping process can be replaced by an extraction–scrubbing–stripping process in which the metal ions are transferred from chloride media to sulfate media. The process involves essentially three steps: 1) extraction of metal ions from chloride solution, 2) scrubbing of chloride ions from the organic phase, and 3) stripping of metal ions from the scrubbed organic phase with sulfuric acid solution.

The purified and concentrated sulfate solutions obtained as a result of the process above are suitable for the classical electrowinning of the metal.

In the three-step solvent process, mixed extractants (one basic or solvating reagent and one chelating reagent) or bi-functional extractants can be used. Some mixtures of extractants are proposed, first of all, for copper(II) recovery from chloride solutions, e.g., an amine and a  $\beta$ -diketone (Kyuchoukov and Mihaylov, 1991; Kyuchoukov and Mishonov, 1993), a hydrophobic pyridine derivative and a hydroxyoxime or a  $\beta$ -diketone (Fletcher et al., 1991; Cierpiszewski and Szymanowski, 2000; Borowiak-Resterna and Szymanowski, 2000). The mixtures containing a basic extractant (e.g., ALAMINE 336) with a chelating extractant (e.g., LIX 54) are suitable for transporting copper(II) from strongly acidic chloride media. The extractant mixtures cannot be used for the selective extraction of copper(II) in the presence of iron(III). If the extractant mixture contains a solvating and a chelating component, then the selective extraction of copper(II) over iron(III) can be carried out. In the first step of the novel process the weak organic base (e.g., ester or amide of pyridinedicarboxylic acid) selectively extracts copper ions from the weakly acidic chloride solution by the solvation mechanism. After scrubbing of chloride ions from the organic phase (metal ions are transferred from the solvate into the chelate) and stripping of metal ions from the organic phase with sulfuric acid, the concentrated copper sulfate solution is obtained. The solution does not contain iron ions.

The recovery of zinc(II) from chloride media is one of the most commonly used hydrometallurgical processes. In chloride media, basic, acidic and solvating reagents were used as zinc(II) extractants (Deep and de Carvalho, 2008; Regel-Rosocka, 2010; Parus et al., 2012;

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Wieszczycka, 2013). Few of them were used for recovery of zinc ions by the extraction–scrubbing–stripping process. The mixture of ACORGA ZNX 50 (a bibenzimidazole-based solvating reagent) and LIX 54 (chelating reagent) was proposed for zinc(II) transfer from weakly acidic chloride solutions (pH ranging between 2 and 3) into sulfate media (Jakubiak et al., 1999). A hydrophobic derivative of bibenzimidazole (an active component of ACORGA ZNX 50) is a very weak base and, therefore, it is not a strong extractant of zinc(II). However, it has the advantage of selective extraction of zinc(II) in the presence of iron(III). For zinc(II) recovery from acid chloride solutions (pH < 1) Kyuchoukov et al. (1997, 1998) proposed the bi-functional extractant Kelex 100, which contains 7-alkyl-8-hydroxyquinoline as the active component.

Hydrophobic esters and amides of pyridinecarboxylic acids for the extraction of copper ions from chloride solutions are proposed by Dalton et al. (1986), Cote et al. (1994), Borowiak-Resterna and Lenarcik (2004). Our previous studies have shown that hydrophobic pyridinecarboxamides can extract zinc ions in systems with varied acidities (Borowiak-Resterna et al., 2010).

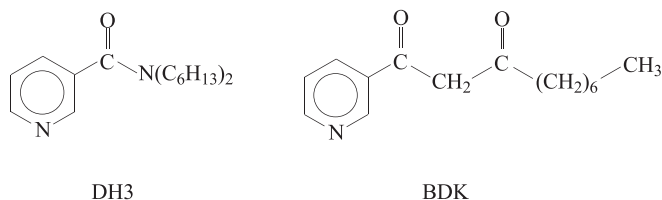
Hydrophobic  $\beta$ -diketones, e.g., commercial extractant LIX 54, are important extractants of copper(II) from ammonia solutions (Kordosky and Virmig, 2002). The extractant is able to extract Zn(II) from aqueous solutions at pH > 5.

It is the objective of this work to present fundamental studies on the transfer of zinc(II) both from weakly acidic and strongly acidic chloride media into sulfate solutions by the mixture of two hydrophobic extractants, N,N-dihexylpyridine-3-carboxamide and 1-phenyldecane-1,3-dione.

## 2. Experimental

### 2.1. Reagents

Two model extractants were used. The structures of the studied compounds are as follows:



N,N-dihexylpyridine-3-carboxamide (DH3) was used as a solvating reagent in weakly acidic chloride media or as a basic extractant which transfers zinc(II) from strongly acidic chloride solutions as ion pairs. The synthesis of the amide was described in an earlier paper (Borowiak-Resterna, 2006).

1-Phenyldecane-1,3-dione (BDK) was used as a chelating reagent. The  $\beta$ -diketone was obtained by the condensation of acetophenone with an excess of ethyl octanoate in the presence of sodium ethylate (Mickler et al., 1992).

The purity of the synthesized compounds in the range 97–99% was determined by GC–MS (Hewlett Packard 5890 Series II with detector MSD HP 5970B). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra prove the structure of the compounds. The spectra were measured on a Varian UNITY 300 spectrometer (500 and 125 MHz, respectively) in CDCl<sub>3</sub> using tetramethylsilane as internal reference.

### 2.2. Extraction procedure

Zinc chloride, hydrochloric acid (36%), sulfuric acid (98%), ammonia (25%), sodium chloride, sodium nitrate (POCH) and lithium nitrate (MERCK) of analytical grade were used to prepare aqueous solutions. Deionized water and toluene of analytical grade (POCH) were used as diluents. Decan-1-ol of analytical grade (Fluka) was used as a modifier.

The zinc(II) extraction, the chloride scrubbing and the zinc(II) stripping were carried out at 20–25 °C. Equal volumes of aqueous and organic phases were shaken in a test tube or in a separatory funnel for 60 min, while the time required for attaining the extraction, scrubbing and stripping equilibrium did not exceed 5 min. The phases were separated. Zinc(II) concentration was determined in the aqueous phase after extraction, scrubbing, and stripping by atomic absorption spectrometry using Z8200 apparatus (Hitachi) or by titration with EDTA in the presence of eriochrome black T. The concentration of zinc(II) ions in the organic phase was determined by mass balance. Extraction percentage (%E) and re-extraction percentage (percentage of stripping) (%R) were calculated from the following equations (assuming that the phase volumes did not change):

$$\%E = \frac{[Zn]_{(o)}}{[Zn]^0} \times 100\% = \frac{[Zn]^0 - [Zn]}{[Zn]^0} \times 100\% \quad (1)$$

$$\%R = \frac{[Zn]^R}{[Zn]_{(o)}} \times 100\% = \frac{[Zn]^R}{[Zn]^0 - [Zn]} \times 100\% \quad (2)$$

where

[Zn]<sup>0</sup> the metal concentration in the aqueous phase before extraction,

[Zn]<sub>(o)</sub> and [Zn] the metal concentration in the organic and aqueous phase after extraction, respectively,

[Zn]<sup>R</sup> the metal concentration in the aqueous phase after stripping (re-extraction).

The confidence interval for [Zn(II)] was estimated for six parallel extraction, scrubbing, and stripping processes, at level of confidence (1 –  $\alpha$ ) = 0.95. It is equal for extraction: [Zn]<sub>(aq)</sub> = 0.00402 ± 0.000034 M, for scrubbing: [Zn]<sub>(aq)</sub> = 0.00125 ± 0.000028 M, for stripping: [Zn]<sup>R</sup> = 0.00672 ± 0.00006 M.

The chloride concentration in the aqueous phase was determined by potentiometric titration with silver nitrate (0.005 M) using 702 SM Titrino (Metrohm). Measurements of pH were made using the 713 pH meter (Metrohm).

### 2.3. Weakly acidic chloride media – the composition of the solutions used

Extraction from weakly acidic chloride solutions was carried out at a constant water activity ( $a_w = 0.835$ ) and a constant total concentration of ions and molecules dissolved in aqueous solution ( $\sigma = 8.0$  M), [NaCl] + [LiNO<sub>3</sub>] + [NaNO<sub>3</sub>] = 4 M. In every extraction experiment, zinc(II) concentration was equal to 0.01 M and pH of the aqueous phase was close to 3.5–3.7. The chloride concentration was varied to be in the range 0.1–4.0 M. The concentration of each extractant (DH3 and BDK) in toluene was 0.2 M.

The ammonia concentration in the aqueous solution used for the scrubbing of chloride ions was varied between 0.005 and 0.03 M. The sulfuric acid concentration in the aqueous solution used for the stripping of zinc(II) was varied between 0.001 and 0.02 M.

### 2.4. Strongly acidic chloride media – the composition of the solutions used

Extraction from strongly acidic chloride solutions was carried out at constant zinc(II) concentration (0.01 M) and constant chloride concentration ([NaCl] + [HCl] = 4 M). The extractants were dissolved in toluene or a mixture of toluene/decan-1-ol (9:1 v/v). The concentration of each extractant (DH3 and BDK) in organic solution was 0.1 M.

The ammonia concentration in the aqueous solution used for the scrubbing of chloride ions was varied between 0.15 and 0.3 M. The sulfuric acid concentration in the aqueous solution used for the stripping of zinc(II) was varied between 0.02 and 0.1 M.

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