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# Pyridineimdamide derivatives - Efficient zinc(II) extractants

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ABSTRACT

Novel extractants, hydrophobic *N′*-alkyloxypyridine-2-, -3- and -4-carboximidamides, were proposed as the efficient zinc(II) extractants from acidic chloride solutions. In this study various factors affecting zinc (II) extraction, such as concentration of chloride ions, mineral acid and zinc in the aqueous feed solution, structure and concentration of the extractant and type of the organic diluent were studied. It was found that the extraction of Zn(II) was observed for the pyridine-3- and 4-carboximidamides with 2-ethylhexyl group and the extraction abilities increased with the increase of chloride ions concentration. *N′*-(2-ethyl hexyloxy)pyridine-4-carboximidamide appeared to be the most efficient extractant, as well as, it was the most suitable in terms of loading capacity. It was also found that 4-EH enabled a complete transfer of Zn (II) from the concentrated aqueous solution by using a two-stage counter-current extraction at an O/A ratio of 7.5 or at O/A = 8 by using a one-stage cross-flow extraction.

## 1. Introduction

Zinc is produced from various primary and secondary materials. The first group includes different types of ore concentrates with a majority zinc base component such as zinc sulfide. The second group consists of waste from industrial processes such as fly ash, galvanic sludge, steel dust and other residues or scrap arising from the processing of alloys and pressure casting [1,2]. The hydrometallurgical route is used for extracting zinc from sulfide, oxide, carbonate or silicate concentrates and also from secondary materials such dusts and fumes from pyrometallurgical processes, from secondary zinc oxides coming from fuming processes like Waelz and Primus furnaces and from spent pickling wastes [3]. For many reasons, hydrometallurgical processes are more environmentally friendly than the pyrometallurgical processes. Advantages include the lack emission of harmful gases, as well as, significantly lower energy inputs necessary to carry out the process [4]. One major problem in the solvent extraction processes is the use of environmentally unfriendly solvents and their release to the environment. This problem can be reduced or even eliminated by using nontoxic and insoluble in water solvents, which can also be easy removed from wastewater. Regardless of ecological aspects, a high selectivity and capacity of this method recommends solvent extraction as a suitable method for the removal of heavy metals from the waste waters [5].

In recent years, it has become increasingly more financially attractive to recover zinc(II) from acidic chloride solutions, which is due to high solubility of zinc(II) chlorides which allows to reach higher concentration of metal in the aqueous solution high ionic activities obtained in concentrated chloride giving high capacities of the extraction and much higher selectivity towards Fe than by using sulfuric acid [6–9]. The extraction of zinc(II) from aqueous solutions, containing chloride ions, may be carried out using various type of extractants: acidic, basic and solvating. The most commonly used acidic extractant is DEHPA (*bis*(2-ethylhexyl) phosphoric acid) [10]. This compound has been widely proposed as a metal extractant in majority of aqueous solutions: sulfate, nitrate, phosphate and chloride [11,12]. Kelex 100 (with 7-alkyl-8-hydroxyquinoline as an active component) can extract Zn(II) in a presence of hydrochloric acid. The downside of the extractant is the necessity to eliminate extracted chloride ions by scrubbing with an aqueous ammonia solution [3,13]. Secondary and tertiary amines, as basic extracting agents, have been also tested to recover Zn(II) from acidic chloride solutions. Among these the most important results have been obtained for Amberlite LA2 [14], Hoe F 2562 [15], Alamine 336 [16], Adogen 364 [3,17] and for a representative of quaternary ammonium salts, Aliquat 336, which extracts zinc mainly as anionic chloro-complexes [18].

Tributyl phosphate (TBP), which belongs to organophosphorus extractants group, is one of the most popular compounds used as solvating extractants. In many researches, a capability of TBP to transfer zinc(II) from chloride solutions has been studied [2,14,15,19]. TBP shows very high extraction efficiency, but a

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stripping effectively occurs without a chloride ions presence - by mixing with water or ammonia solution. Other organophosphorous compounds such as dibutyl butylphosphonate [20] and trialkylphosphine oxides (TOPO, Cyanex 923) [21–23] have ability to remove zinc(II) from various chloride solutions but with low selectivity. Cyphos IL 101 and Cyphos IL 104, which represent a phosphonium ionic liquid, have been successfully evaluated as potential extractants of zinc(II) from HCl [24,25]. This type of extractants extracts zinc(II) as $ZnCl_4^{2-}$ with a high yield but a selectivity towards Fe(II) and Fe(III) is low.

Hydrophobic pyridylketoximes, have also been proposed as zinc extractant, but in the case of the acidic chloride solutions only 3-pyridylketoxime with decyl alkyl chain (3PC10) can be used as the zinc extractant, also in the presence of other metals such as iron(II) and iron(III) [26]. The disadvantages of this process include high acidity of the aqueous feed and long shaking time, which are required to extract Zn(II) not only as $ZnCl_2$ but also as $ZnCl_3^-$ and $ZnCl_4^{2-}$. Much higher efficiency of the 3-pyridylketoxime towards zinc(II) in HCl has been observed using membrane separation system such as a pseudo-emulsion based hollow fiber strip dispersion method (PEHFSD) [27] and after a quaternisation with propyl bromide [28]. However, in the case of 3-[1-(hydroxyimino)undecyl]-1-propylpyridinium bromide the selectivity decreases with the increase of HCl concentration.

Despite the wide range of available complexing agents, it is difficult to find compound being an effective extractant of zinc(II) from chloride solution, especially from spent pickling baths, therefore, the development of novel extracting agent is the most crucial in current studies. The coordination capability of pyridineimidamides reported in the literature concern mainly on *N*′-hydroxy pyridine-2-carboximidamide, which has the ability to complex Zn(II), Cd(II), Cu(II) and Ni(II) at a different pH [29–31]. This compound is capable to coordinate to the metal mainly via the pyridine and imine nitrogens, having also the unique hydrogen bonding potential of the amine group (formation $NH^-$). It was also shown that *N*′-hydroxypyridine-2-carboximidamide have pronounced tendency to form polynuclear complexes, especially if hydroxide or nitrate ions are concerned.

The aim of this paper is to study the extraction of zinc(II) from acidic chloride solutions using novel extractants - the hydrophobic *N*′-alkyloxypyridine-2-, -3- and -4-carboximidamides.

## 2. Experimental

### 2.1. Reagents

All reagents used in this study were of reagent grade. Toluene (99.8%; POCH; Poland) heptane (99.8%; POCH; Poland) and decan-1-ol (>99%; Merck; Germany) were used as components of the organic phase. Sodium chloride (ACS reagent; Sigma-Aldrich, Germany), lithium chloride (ACS reagent; Sigma-Aldrich, Germany), sodium nitrate (ACS reagent; Sigma-Aldrich; Germany), hydrochloric acid (38%) (AR reagent; POCH; Poland), nitric acid (70%) (AR reagent; POCH; Poland), zinc(II) chloride (anhydrous) (ACS reagent; Sigma-Aldrich; Germany) and zinc(II) nitrate (hexahydrate) (ACS reagent; Sigma-Aldrich; Germany) were used to compose the aqueous phase.

### 2.2. Synthesis of extractants

Synthesis of *N*′-alkyloxypyridine-2-, -3- and -4-carboximidamides was in a two-stages reaction (Fig. 1). In first stage three constitutional isomers were obtained by treating 2-, 3- or 4-pyridinecarbonitrile with hydroxylamine hydrochloride in the presence of sodium hydroxide. Used solvent was ethanol and the reaction was leading at the boiling temperature of solvent by 1 h. After filtration and recrystalization from ethanol/water white crystals was obtained. In the second stage proper pyridinecarboxamidoximes was treated by two different alkylating agents: decyl bromide or ethylhexyl bromide to obtain final *N*′-alkyloxypyridine-2-, -3- and -4-carboximidamides. First step of this synthesis was to form sodium salt of pyridinecarboxamidoximes by reaction with sodium hydroxide in isopropanol/water for 0.5 h. Next an alkyl halide was added to yield the alkylation reaction product. The equimolar ratio of the reactants was used in the isopropanol as a solvent by 2.5 h in the boiling temperature of a solvent.

*N*′-(2-ethylhexyloxy)pyridine-2-carboximidamide (**2-EH**): yield 48%; b.p. = 80–81 °C (0.6 mmHg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.91–0.96 ($CH_3$, dd, 6H); 1.34–1.50 ($CH_2$, m, 8H); 1.72–1.75 (CH, ttt, 1H); 4,04–4,06 ($OCH_2$, d, 2H); 5.64 ($NH_2$, s, 2H); 7.28–7.29 ($H_{py}$, dd, 1H); 7.69–7.01 ($H_{py}$, dd, 1H); 7.99–8.01 ($H_{py}$, d, 1H); 8.54 ($H_{py}$, d, 1H).

*N*′-(2-ethylhexyloxy)pyridine-3-carboximidamide (**3-EH**): yield 32%; b.p. = 119–120 °C (0.6 mmHg); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.91–0.96 ($CH_3$, dd, 6H); 1.34–1.50 ($CH_2$, m, 8H); 1.72–1.75 (CH, ttt, 1H); 4,04–4,06 ($OCH_2$, d, 2H); 5,64 ($NH_2$, s, 2H); 7.54–7.55 ($H_{py}$, dd, 1H); 7.60–7.61 ($H_{py}$, d, 1H); 8.53–8.55 ($H_{py}$, d, 1H); 8.85–8.83 ($H_{py}$, s, 1H).

*N*′-(2-ethylhexyloxy)pyridine-4-carboximidamide (**4-EH**): yield 22%; b.p. = 149–151 °C; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.91–0.95 ($CH_3$, dd, 6H); 1.33–1.48 ($CH_2$, m, 8H); 1.71–1.74 (CH; ttt, 1H); 4.06–4.08 ($OCH_2$, d, 2H); 5.01 ($NH_2$, s, 2H); 7.75–7.77 ($H_{py}$, d, 2H); 8.65–8.66 ($H_{py}$, d, 2H).

*N*′-decyloxypyridine-2-carboximidamide (**2-D**): yield 50%; b.p. = 154–156 °C, $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.87–0.90 ($CH_3$, t, 3H); 1.15–1.16 ($CH_2$, kt, 2H); 1.28–1.43 ($CH_2$, m, 12H); 1.70–1.77 ($CH_2$, tt, 2H); 4.13–4.16 ($OCH_2$, t, 2H); 5.75 ($NH_2$, s, 2H); 7.34–7.37 ($H_{py}$, dd, 1H); 7.75–7.79 ($H_{py}$, dd, 1H); 8.08–8.10 ($H_{py}$, d, 1H); 8.55–8.53 ($H_{py}$, d, 1H).

*N*′-decyloxypyridine-3-carboximidamide (**3-D**): yield 41%; b.p. = 130–133 °C, $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.87–0.90 ($CH_3$, t, 3H); 1,27 ($CH_2$, m, 10H); 1.55–1.59 ($CH_2$, tt, 2H); 1.70–1.74 ($CH_2$, tt, 2H); 3.62–3.65 ($CH_2$, tt, 2H); 4.11–4.15 ($OCH_2$, t, 2H); 4.91 ($NH_2$, s, 2H); 7.54–7.55 ($H_{py}$, dd, 1H); 7.60–7.61 ($H_{py}$, d, 1H); 8.63–8.65 ($H_{py}$, d, 1H); 8.82–8.83 ($H_{py}$, s, 1H).

*N*′-decyloxypyridine-4-carboximidamide (**4-D**): yield 37%; b.p. = 114–116 °C, $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 0.87–0.90 ($CH_3$, t, 3H); 1.15–1.16 ($CH_2$, kt, 2H); 1.28 ($CH_2$, m, 10H); 1.41–1.43 ($CH_2$, tt, 2H); 1.72–1.77 ($CH_2$, tt, 2H); 4.13–4.16 ($OCH_2$, t, 2H); 5.75 ($NH_2$, s, 2H); 7.75–7.77 ($H_{py}$, d, 2H); 8.55–8.56 ($H_{py}$, d, 2H).

### 2.3. Extraction procedure

The basic studies were carried out at a constant zinc(II) concentration equal to 0.01 mol/L. Aqueous feed solutions were prepared by dissolving in ultrapure water an appropriate amounts of $Zn(NO_3)_2$ (nitrate solution) or $ZnCl_2$ (chloride or chloride/nitrate solutions), $NaNO_3$, $LiNO_3$, $HNO_3$ (or HCl) and NaCl. Extraction equilibrium studies were carried out:

- at a constant ionic strength (I = 4 mol/L) and various HCl and NaCl concentrations (from 0 to 4 mol/L);
- at a constant mineral acid concentration ($HNO_3$; 0.5 mol/L), constant $a_w = 0.835$, constant ionic strength (I = 4 mol/L) and various chloride ion concentrations (from 0 to 4 mol/L). The ionic strength was adjusted by appropriate addition of NaCl, $NaNO_3$ and $LiNO_3$ (Table 1).