Zinc(II) and Iron(III) Extraction From Chloride Media Using Pyridinecarboximidamides as Extractant

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The aim of the study was to investigate the extraction properties of new hydrophobic pyridine derivatives - pyridinecarboximidamides. This work was focused on two compounds which are their constituent isomers: *N'*-(2-ethylhexyloxy)pyridine-3-carboximidamide (Eh-3IA) and *N'*-(2-ethylhexyloxy)pyridine-4-carboximidamide (Eh-4IA). The study included determining the effect of initial pH, chloride ion concentration, metal ion concentration and ligand concentration on the extraction efficiency. The ability of both ligands to separate zinc(II) ion from the solution containing iron(III) was also examined.

1. Introduction

Solvent extraction is a separation method based on formation of complex compounds between ligand molecules and metal ions. Liquid-liquid extraction involves intensive contact of an organic phase containing an extractant diluted and charged water phase [1]. During the extraction process, extractant molecules bond metal ions and transfer obtained complex to the organic phase. Metal ions are recovered from an organic phase by reextraction. The final step is to purify the concentrated metal solution, for example by electrolysis [2].

Nowadays, solvent extraction is an important method used in hydrometallurgical processes but also is a method for metal recovery from waste solutions. The development of industry is a source of an increasing volume of wastewaters containing metal ions at various concentrations. Recovery of metal ions from wastewaters is one of the most important tasks due to a depletion of natural resources and the increasing demand for high-purity metal. In addition, it is significant because of the toxic nature of heavy metals to the environment, including plants, animals and humans [3,4].

Ideal extractant should not only provide the purification of wastewaters, but also enable to quick and selective recover of high-purity metals with a considerable efficiency. The study purpose was to define the extraction properties towards Zn(II) and Fe(III) of novel hydrophobic pyridine derivatives: *N'*-(2-ethylhexyloxy)pyridine-3-carboximidamide (Eh-3IA) and *N'*-(2-ethylhexyloxy)pyridine -4-carboximidamide (Eh-4IA, Figure 1).

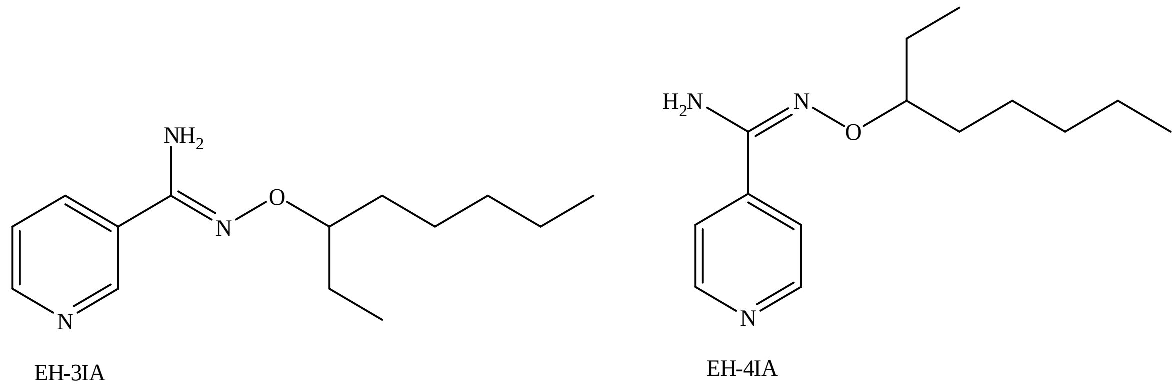

Figure 1. *N'*-(2-ethylhexyloxy)pyridine-3-carboximidamide (Eh-3IA) and *N'*-(2-ethylhexyloxy)pyridine-4-carboximidamide (Eh-4IA)

2. Experimental

2.1 Reagents

All reagents used in this study were of reagent grade. Toluene (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), hydrochloric acid (38%) (AR reagent; POCH; Poland), zinc(II) chloride (anhydrous) (ACS reagent; Sigma-Aldrich; Germany) and iron(III) chloride (hexahydrate) (ACS reagent; Sigma-Aldrich; Germany) were used to compose the aqueous phase.

2.2 Extraction procedure

Aqueous feed solutions were prepared by dissolving in ultrapure water appropriate amounts of $ZnCl_2$, $FeCl_3$, HCl and NaCl. Extraction equilibrium studies were carried out at constant ionic strength (I = 4 mol/L) and various HCl and NaCl concentrations (from 0 to 4 mol/L). Another type of the aqueous phase was feed solution prepared with 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 water activity was adjusted by appropriate addition of NaCl, $NaNO_3$ and $LiNO_3$ (Table 1). The concentrations of the *N'* -alkyloxypyridinecarboximidamides in the organic phase were changed from 0.02 to 0.1 mol/L. Concentration of the metal were changed from 0.02 to 0.12 mol/L. Extraction experiments were carried out in test tubes using equal volumes of both phases (O/W = 1). Both phases were mechanically shaken at room temperature (20-22^{0}C) using Bio-mix BWR 04. The metal concentration in the aqueous phase was analyzed with atomic absorption spectrometry AAS (HITACHI Z-8200 Polarised Zeeman).

3. Results and Discussion

3.1 Zinc(II) and iron(III) extraction

N'-(2-ethylhexyloxy)pyridine-3-carboximidamide (Eh-3IA) and *N'*-(2-ethylhexyloxy)-pyridine-4-carboximidamide (Eh-4IA) were examined for their ability to extract zinc(II) and iron(III) from aqueous solution containg HCl and NaCl. Figures 2 and 3 show the results of the study.

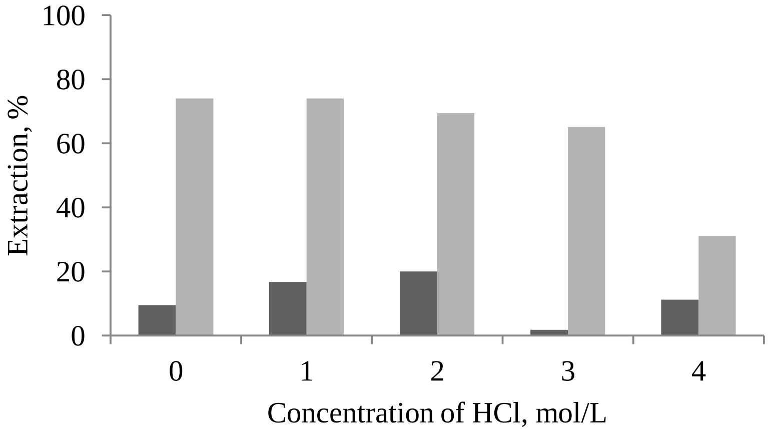

Figure 2. Influence of HCl concentration on extraction of zinc(II) (light grey) and iron(III) (dark grey) using Eh-3IA as extractant ([extractant]=0.1 mol/L; $[Zn^{2+}]$=0.01 mol/L; $[Fe^{3+}]$=0.01 mol/L; $[Cl^{-}]$=4 mol/L; a_w=0.835)

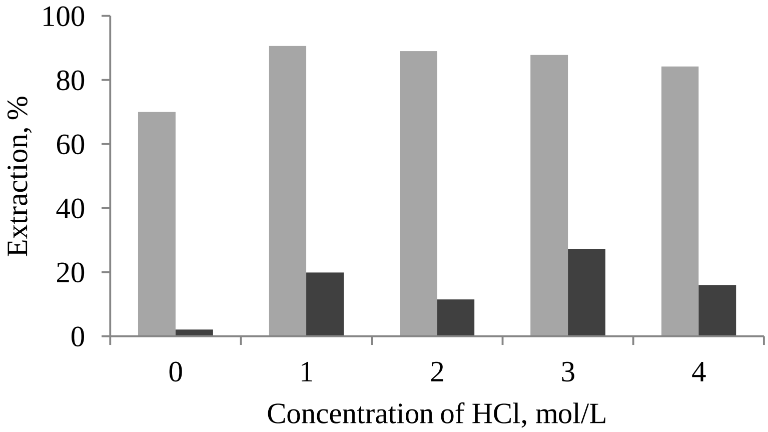

Figure 3. Influence of HCl concentration on extraction of zinc(II) (light grey) and iron(III) (dark grey) using Eh-4IA as extractant ([extractant]=0.1 mol/L; $[Zn^{2+}]$=0.01 mol/L; $[Fe^{3+}]$=0.01 mol/L; $[Cl^{-}]$=4 mol/L)

The obtained results show that both reagents have good extraction abilities towards zinc(II). At concentration of 1 mol/L HCl, Eh-3IA extracts zinc(II) in 74%, while Eh-4IA in 91% concentration. However, at the same conditions both reagents show much less extraction abilities towards iron(III) (20% and 17% for Eh-4IA and Eh-3IA, respectively). The difference in the extraction properties towards Fe(III) and Zn(II) can enable separation of both metals, especially using as the extractant Eh-3IA and conducting extraction from solution containing 3 mol/L HCl.

3.2 Effect of chloride ion concentration

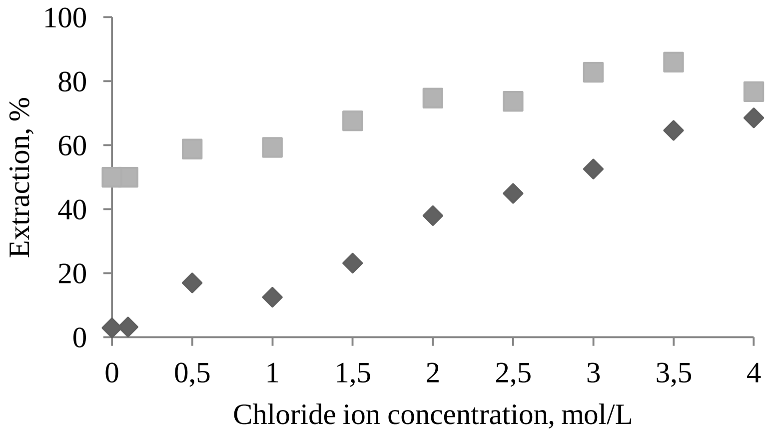

Figure 4. Effect of chloride ion concentration on extraction of zinc(II) with Eh-4IA (light grey) and Eh-3IA (dark grey) ([extractant]=0.1 mol/L; $[Zn^{2+}]$=0.01 mol/L; $[Cl^-]$=0-4 mol/L; a_w=0.835; $[HNO_3]$ = 0.5 mol/L; I = 4 mol/L)

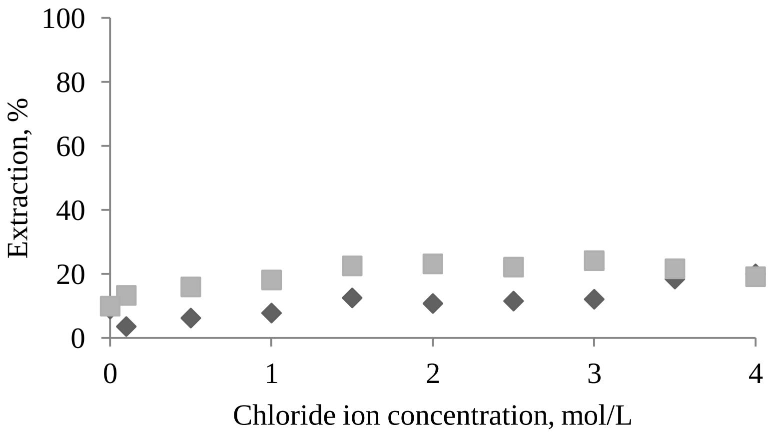

Figure 5. Effect of chloride ion concentration on extraction of iron(III) with Eh-4IA (light grey) and Eh-3IA (dark grey) ([extractant]=0.1 mol/L; $[Fe^{3+}]$=0.01 mol/L; $[Cl^-]$=0-4 mol/L; a_w=0.835; $[HNO_3]$ = 0.5 mol/L; I = 4 mol/L)

The effect of the chloride ion concentration on the zinc(II) and iron(III) extraction was examined using the aqueous solutions containing, besides 0.01 mol/L Zn(II) or Fe(III), a constant mineral acid concentration ($[HNO_3]$ = 0.5 mol/L), constant water activity (a_w = 0.835), constant ionic strength (I = 4 mol/L) and various chloride ion concentrations (from 0 to 4 mol/L NaCl). The obtained results given in Figure 4 show that in the case of both Eh-3IA and Eh-4IA the zinc(II) extraction increases with the increase of the chloride ion concentration. Moreover, results indicate that Eh-3IA is less efficient than Eh-4IA, but the difference decreases when chloride ion concentration increases.

In the case of the Fe(III) the experimental results clearly show that, even after contact with the concentrated chloride solution, the extraction does not exceed 25% (Figure 5).

3.3 Effect of extractant concentration on extraction

The effect of Eh-3IA and Eh-4IA concentration on zinc(II) and iron(III) extraction was studied using the aqueous feed solutions containing the constant concentration of zinc(II) or iron(III) (0.01 mol/L), constant concentration of chloride ion (3.5 mol/L) and the constant concentration of nitric acid (0.5 mol/L). The concentration of Eh-3IA and Eh-4IA in toluene with 10% (v/v) addition of decan-1-ol varied in the range of 0.01 ─ 0.1 mol/L.

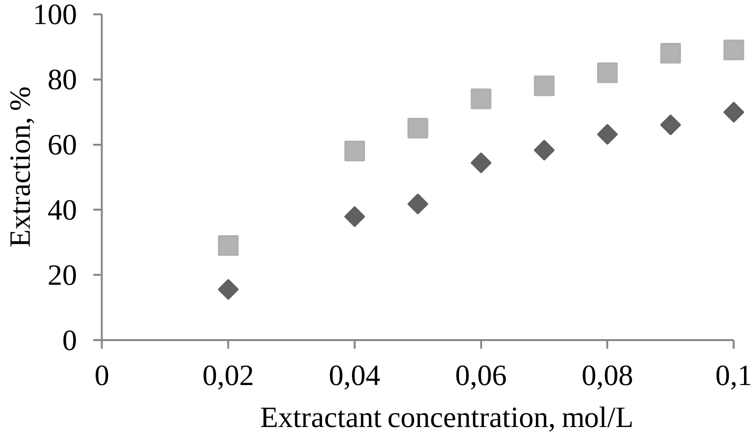

Figure 6. Effect of extractant concentration on extraction of zinc(II) with Eh-3IA (dark grey) and Eh-4IA (light grey) ([extractant]=0.02-0.1 mol/L; $[Zn^{2+}]$=0.01 mol/L; $[Cl^{-}]$= 3.5 mol/L; a_w=0.835; $[HNO_3]$ = 0.5 mol/L; I = 4 mol/L)

As it can be observed in Figure 6, the increasing concentration of the extractant accelerates the zinc extraction. The observed dependence is comparable for both studied reagents. For example, the reduction of the extractant concentration from 0.1 to 0.5 mol/L causes decrease of the extraction from 89% to 65% for Eh-4IA and from 70% to 42% for Eh-3IA.

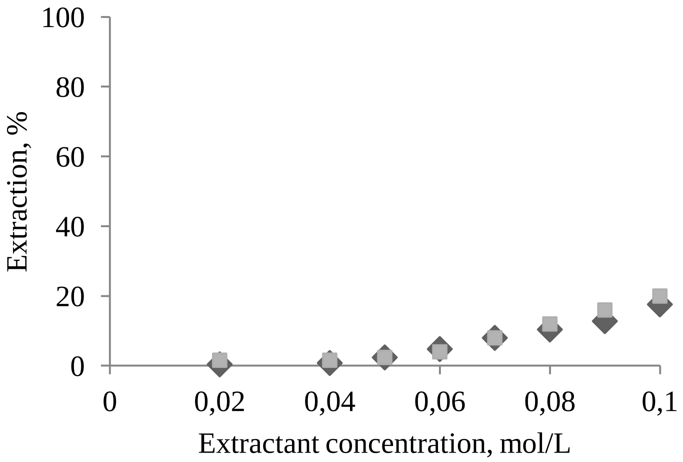

Figure 7. Effect of extractant concentration on extraction of iron(III) with Eh-3IA (dark grey) and Eh-4IA (light grey) ([extractant]=0.02-0.1 mol/L; $[Fe^{3+}]$=0.01 mol/L; $[Cl^{-}]$=3.5 mol/L; a_w=0.835; $[HNO_3]$ = 0.5 mol/L; I = 4 mol/L)

As Figure 7 shows, the increasing concentration of the extractant causes slightly increase in the iron(III) extraction and it does not exceed 20%.

3.4 Effect of zinc(II) and iron(III) ion concentration

The effect of zinc(II) and iron(III) concentration on the extraction was studied over the range of Zn(II) and Fe(III) 0.01 – 0.1 mol/L at the constant concentration of NaCl (4 mol/L) and constant concentration of HCl (0.5 mol/L). In the extraction data presented in Figure 8, regardless on used extractant the increasing Zn(II) concentration decreases the extraction from 95 to 41% for Eh-4IA and from 76 to 35% for Eh-3IA. It was also determined maximum capacities of the studied extractants. In the case of *N'*-(2-ethylhexyloxy)pyridine-4-carboximidamide capacity is approximately 0.49 mol of Zn(II) per 1 mol of the imidamide, while *N'*-(2-ethylhexyloxy)pyridine-3-carboximidamide has ability to extract maximum is 0.41 mol of Zn(II) per mol of the imidamide.

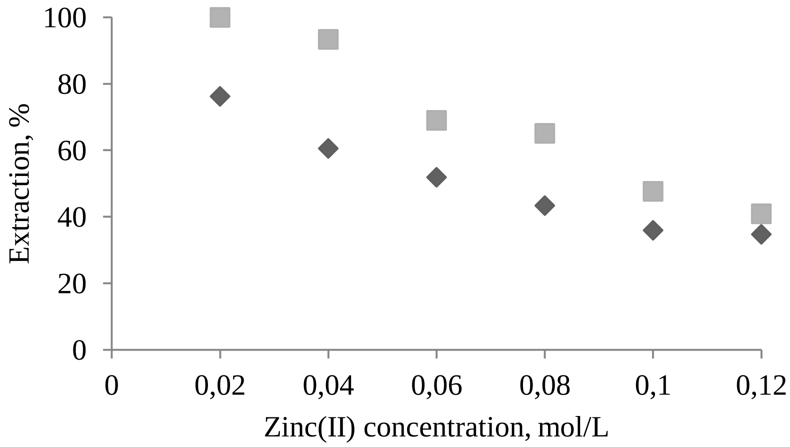

Figure 8. Effect of zinc(II) concentration on extraction with Eh-4IA (light grey) and Eh-3IA (dark grey) ([extractant]=0.1 mol/L; $[Zn^{2+}]$=0.02-0.12 mol/L; [NaCl]=3.5 mol/L; [HCl]=0.5 mol/L)

The experimental data presented in Figure 9 concern Fe(III) extraction. The results indicate very low extraction, which also decreases with the increase in the Fe(III) concentration.

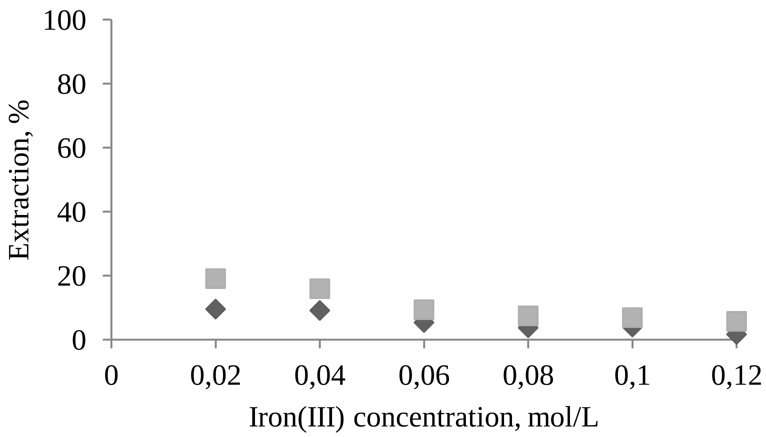

Figure 9. Effect of iron(III) concentration on extraction with Eh-4IA (light grey) and Eh-3IA (dark grey) ([extractant]=0.1 mol/L; $[Fe^{3+}]$=0.02-0.12 mol/L; [NaCl]=3.5 mol/L; [HCl]=0.5 mol/L)

4. Conclusion

The obtained results confirmed the ability of the studied compounds to extract zinc(II) from acidic solutions, however, their abilities to complex iron(III) and next its transfer to the organic phase were low over the whole concentration range of HCl, extractant and Fe(III). The study confirmed positive influence of chloride and extractant concentrations on the zinc(II) extraction. Furthermore, Eh-4IA appeared as a more effective extractant for zinc(II) and iron(III) than Eh-3IA.

Acknowledgement

This study was funded by National Science Center Poland research grant funds according to decision No. DEC-2015/17/N/ST8/00285. Financial support through the 03/32/DSMK/0720 grant was also acknowledged.

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