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Solvent extraction of zinc(II) ions from chloride media by 4-pyridylketoximes

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Abstract: Three homologues of 4-pyridylketoximes were synthesized and used as potential ligands for zinc(II). Their solvent extraction behaviors for zinc(II) in chloride solutions were investigated using $CHCl_3$ as the diluent. The effect of different variables on the extraction of zinc(II) ions, such as the pH of aqueous phase, metal and chloride ions as well as the type of oxime, has been investigated. Results indicated that 4-pyridylketoximes could extract zinc(II) ions from chloride solutions and the extraction depended on the concentrations of the ligand, chloride ions and hydrochloride acid. Slope analysis confirmed that the 4-pyridylketoximes ligands form a 1:2 complex with zinc(II) in both chloride/nitrate and chloride/perchlorate solutions. After extraction, zinc(II) could be easily stripped from organic phase with water.

Keywords: solvent extraction, pyridylketoxime, zinc(II), recovery, chloride media

1. Introduction

Zinc is an important metal required for various applications in metallurgical, chemical and textile industries. Approximately 30% of global zinc production arises from secondary zinc materials such as smelter wastes, spent batteries, galvanizing pickle liquors, waste water streams from fiber manufactures, electroplating processes, etc., which also contain different levels of impurities depending on their sources.

Extraction is very useful for a wide range of applications, such as separation, preconcentration or enrichment of metals prior to determination by an appropriate analytical technique. Solvent extraction is also a useful method to remove metal ions from an aqueous solution to organic solvents and/or complexing agents which are immiscible with water.

The removal of zinc(II) ions from chloride solutions is very important in the industry. Different reagents, such as TBP, Kelex 100 [1], ACORGA ZNX50 [2,3], Cyanex 302 [4], Aliquat 336 and secondary amines [5–7], have been investigated. However, there is still a need to search for new extractants which will effectively remove zinc(II) ions, especially from multicomponent solutions.

Pyridyl aldo- and ketoximes are popular ligands in coordination chemistry [8–11]. The hydrophobic pyridylketoximes are considered to be prospective for removal and separation of metals. Hampl *et al.* [12] have proposed 2-pyridylketoximes as a ligands in membrane transportation of nickel(II).

Hydrophobic oximes of 2- and 4-pyridylketones were proposed to extract metal ions such as copper(II), cadmium(II), iron(III) and zinc(II) from chloride solutions [13–17]. These reagents were also used to remove copper(II) from ammonium chloride, hydrochloric solutions, sulphate and sulphate/chloride [18,19]. These studies showed the influence of the extractant structure, the type of diluents and presence of nitrate and chloride ions in aqueous feed on metal extraction.

The extraction of cadmium(II) ions was observed only with 2-pyridylketoxmies and depended on several aspects, such as solvent type, ligand concentrations and chloride ions concentration [14]. In next work, Parus *et al.* [15] reported data regarding iron(III) extraction from chloride solutions by reagents with a functional group in position 2 and 4 in the pyridine ring and possible separation of copper(II) and iron(III) ions from mulitielemental solutions. The current study shows that 2-pyridylketoximes could be used to extract zinc(II) ions from chloride solutions and that separation of copper(II) ions from mulielemental media is possible. The zinc(II) extraction percent depended on ligand and chloride ions concentration. At low chloride ions concentration an increase of extraction percentage was observed and at higher Cl^- concentration the complex-forming potential of 2-pyridylketoximes slowly decreased [16].

The aim of this study was to investigate the extraction of zinc(II) ions from aqueous solutions with 4-pyridylketoximes. The effect of pH, type of salts (salting-out effects), chloride ions concentration, the composition of the extracting agent and organic diluents have been investigated.

2. Experimental

2.1. Synthesis of model extractant

Oximes of hydrophobic 4-pyridylketones with decyl, dodecyl and tetradecyl alkyl chain (Table 1) were obtained in a two-stage reaction, as described earlier [8,20].

In the first stage, the 4-pyridylketones were synthesized by a reaction of pyridinecarbonitryle with alkyl magnesium bromide in diethyl ether (which was used as a diluent). In the second stage, the oximation reaction of the alkyl-pyridylketones was conducted by using hydroxylamine hydrochloride in ethanol solutions in the presence of Na_2CO_3.

Yields of the synthesized hydrophobic oximes reached 70%. Purities of ketones and oximes were at 98.9% (LC/MS). FT-IR and NMR (^1H, ^{13}C) spectra were used to confirm the structure of the compounds.

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Table 1. Structures of pyridylketoximes.

Abbreviation	Structure	Name
4PC10		1-(4-pyridyl)undecane-1-one oxime
4PC12		1-(4-pyridyl)tridecane-1-one oxime
4PC14		1-(4-pyridyl)pentadecane-1-one oxime

2.2. Extraction procedure

The extraction of zinc(II) chloride by 4-pyridylketoximes was carried out at:

– constant water activity a_w = 0.835 and ionic strength I = 4 mol/L, σ = 8 mol/L, where NaCl, LiNO$_3$ and NaNO$_3$ were used to adjust of water activity and the ionic strength,

– a_w = 0.835, I = 4 mol/L, σ = 8 mol/L, where NaCl and NaClO$_4$ were used to adjust the activity of water and ionic strength,

– a_w = 0.966, I = 1 mol/L, σ = 2 mol/L, where NaCl and NaClO$_4$ were used to adjust the activity of water and ionic strength.

In the experiments, the chloride ions concentrations were changed: from 0.01 to 4 mol/L for I = 4.0 mol/L and from 0.01 to 1 mol/L for I = 1.0 mol/L. The pH value of the aqueous phase was changed from 2 to 7 using 0.2 mol/L solutions of NaOH or HCl. The influence of chloride ions and the concentration of extractants was investigated under constant concentration of zinc(II) ions equal to 0.01 mol/L. In the loading tests, the concentrations of zinc(II) ions were changed from 0.01 to 0.3 mol/L. The second step of the study was focused on investigating the influence of hydrochloric acid concentration on zinc(II) extraction and examined the ability of 4-pyridylketoximes to transfer hydrochloric acidic to the organic phase.

In the solvent extraction studies, the concentrations of extractants were changed from 0.01 to 0.1 mol/L. The extraction was carried out in a small scale at the volume ratio of organic /aqueous phases equal to 1. The phases were mechanically shaken for 30 min and left to separate. The stripping of zinc(II) ions was carried out with pure water, 5% HCl and 5% ammonia solutions. The second step of this study determined the possibility to selectively separate zinc(II) ions from solutions which also contained copper(II) or cadmium(II) ions.

The concentration of zinc(II) ions in the aqueous feed was determined by potentiometric titration with EDTA (Mettler Toledo titrator). When zinc(II) ions were present together with cadmium(II) and copper(II) ions, the content of metals was determined by the ICP-OES technique.

2.3. Calculations

The concentration of metal ions in the organic phase was calculated based on the difference between the metal ion concentrations in the aqueous phase before and after extraction. The distribution coefficient (D) is defined as the ratio of the zinc(II) concentrations in the organic phase to the metal concentration in the aqueous phase. The extraction percentage (%E) of each metal was calculated using the following equation:

$$\%E = \left(\frac{[Zn^{2+}]}{[Zn^{2+}]_o} \right) \cdot 100\% \qquad (1)$$

where: $[Zn^{2+}]$ and $[Zn^{2+}]_o$ denote the metal concentration at an equation in the aqueous and the initial metal concentration in that phase, respectively.

3. Results and discussion

3.1. The effect of organic diluents on zinc(II) extraction

The extraction of zinc(II) ions with 1-(4-pyridyl)undecane-1-one oxime, 1-(4-pyridyl)tridecane-1-one oxime and 1-(4-pyridyl)pentadecane-1-one oxime in solutions with a varying polarity of diluents was studied (Table 2). Good solubility of

Table 2. The extraction of zinc(II) ions with 4-pyridylketoximes ($[Zn^{2+}]$ = 0.010 mol/L, $[Cl^-]$ = 1.0 mol/L (chloride/nitrate), [oxime] = 0.10 mol/L).

Diluent	Percent extraction %E		
	4PC10	4PC12	4PC14
Chloroform	52.2	65.0	67.0
Toluene + 10% v/v decan-1-ol	0	0	0
Isooctane + 10% v/v decan-1-ol	0	0	0
Heptane + 10% v/v decan-1-ol	0	0	0
Exssol 220/230 + 10% v/v decan-1-ol	0[+]	0[+]	0[+]

[+] Concentration of extractant (0.05 mol/L).

4-pyridylketoximes was observed only in chloroform. The solubility of pyridylketoximes in other diluents, such as heptane, isooctane, toluene and Exssol 220/230, was limited. The addition of 10% (v/v) of decan-1-ol increased the solubility of these reagents in isooctane, toluene and heptane, but not in Exssol 220/230.

The results indicated that only chloroform was useful for zinc(II) extraction among the tested solvents. Chloroform exhibited the most rapid separation of phases. The highest extraction degree was observed for 1-(4-pyridyl)tridecane-1-one oxime (4PC12) and 1-(4-pyridyl)pentadecane-1-one oxime (4PC14), and was equal to 65% and 67%, respectively, however when 1-(4-pyridyl)undecane-1-one oxime (4PC10) was used, the extraction degree was equal to 52%. Chloroform was used as the diluent during subsequent experiments.

3.2. The effect of pH and HCl concentration on extraction of zinc(II)

The effect of pH on the extraction of zinc(II) ions from chloride solutions with 1-(4-pyridyl)pentadecane-1-one oxime was investigated at pH range of 1.9–7. The obtained results are shown in Figure 1. The obtained results suggest that the pH did not affect the removal of zinc(II) ions. However, for solutions with pH below 2, complexes of 4-pyridylketoxime with zinc(II) ions precipitated. The ability of solutions with a pH below 4 to carry H^+ ions (0.1–4 mol/L) to the organic phase required further examinations and the results are shown in Table 3. In case of the 1-(4-pyridyl)tridecane-1-one oxime, HCl was transferred to the organic phase in 0.008 mol/L just above 4.0 mol/L HCl in aqueous phase. For lower concentration of HCl in the aqueous phase, the 1-(4-pyridyl)tridecane-1-one oxime did not transport the acid to the organic phase. The amount of HCl transferred to the organic phase was also affected by the chain length of the oxime group.

The 4-pyridylketoxime with a decyl chain transferred the acid to the organic phase in the whole range of hydrogen ions concentration (0.010 mol/L for initial concentration of HCl = 0.10 mol/L and 0.10 mol/L H^+ for concentration 4.0 mol/L HCl).

The 1-(4-pyridyl)pentadecane-1-one oxime forms stable emulsion even after exposure to low concentrations of the acid.

The extraction of zinc(II) from hydrochloride solutions was also investigated (Table 4). In this experiment, the concentration of hydrochloric acid was changed from 0.10 to 4.0 mol/L. The obtained results showed that the extraction degree of zinc(II) ions was constant in the whole investigated range of hydrochloric acid concentrations. The 1-(4-pyridyl)undecane-1-one oxime removed 45% of zinc(II) from the aqueous phase and 1-(4-pyridyl)tridecane-1-one oxime removed 50%, how-

Table 3. Hydrochloric acid content in organic phases depending on the concentration in the aqueous phase ([oxime] = 0.10 mol/L).

Aqueous phase	HCl concentration mol/L		
	Organic phase		
	4PC10	4PC12	4PC14
0.1	0.01	0	
0.5	0.01	0	
1.0	0.02	0	emulsion
2.0	0.07	0	
3.0	0.07	0	
4.0	0.10	0.008	

Table 4. Influence of hydrochloric acid concentration on zinc(II) ions extraction ($[Zn^{2+}]$ = 0.010 mol/L, [oxime] = 0.10 mol/L).

HCl concentration (mol/L) in aqueous phase	Percent extraction %E		
	4PC10	4PC12	4PC14
0.1	45.00*	50.00*	
0.5	45.00*	52.30*	
1.0	49.50*	50.60*	emulsion
2.0	44.80*	54.10*	
3.0	45.50*	49.10*	
4.0	47.60*	50.10*	

* Complex precipitated.

Figure 1. Distribution coefficient of zinc(II) ions versus pH ($[Zn^{2+}]$ = 0.010 mol/L, $[Cl^-]$ = 1.0 mol/L (chloride/nitrate), [4PC14] = 0.10 mol/L).
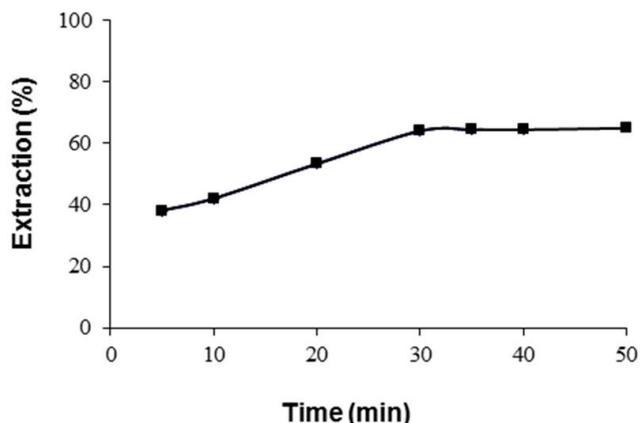
Figure 2. Influence of contact time on extraction of zinc(II) ions from chloride solution by chloroformic solution of 1-(4-py-ridyl)pentadecane-1-one oxime ($[Cl^-] = 1.0$ mol/L, $[Zn^{2+}] = 0.010$ mol /L, [oxime] = 0.10 mol/L).

ever the complexes precipitated in the organic phase during the extraction process for both used oximes.

3.3. Effect of contact time

The effect of contact time on the extraction of zinc(II) ions from chloride media by 1-(4-pyridyl)pentadecane-1-one oxime in chloroform was presented in Figure 2.

The effect was studied by using a varying contact time from 5 to 50 min in a separate experiment. The extraction of zinc(II) ions with 4-pyridylketoximes was rapid, however the contact time of at least 30 min was necessary in order to obtain the highest extraction percent. Phase separation after extraction was very fast and no formation of emulsions was observed.

3.4. Influence of chloride ions, ionic strength and salting-out agents on the extraction

The influence of chloride ions concentration on the extraction zinc(II) ions was established based on the obtained results regarding the extraction of zinc(II) ions from chloride/nitrate solutions (I = 4.0 mol/L) with chloroformic solutions
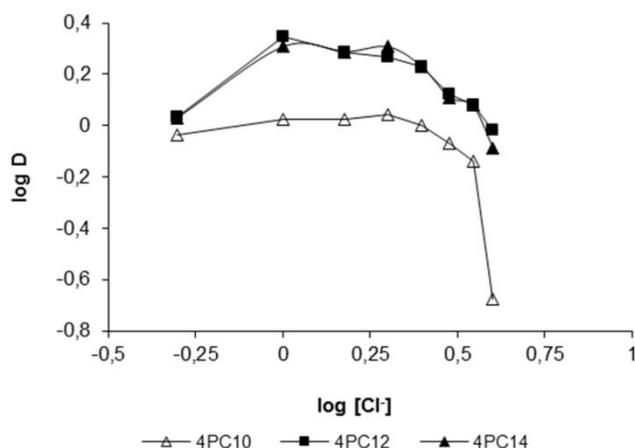
Figure 3. Dependence of chloride ions concentration on zinc(II) ions distribution ratio for 4-pyridylketoximes ($[Zn^{2+}]$ = 0.010 mol/L, a_w = 0.835 (chloride/nitrate ions), [oxime] = 0.10 mol/L).
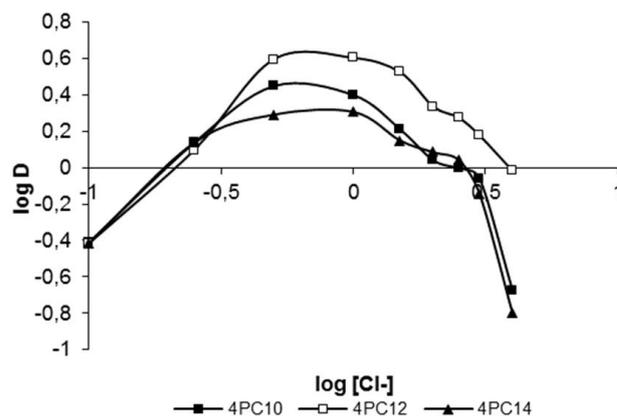
Figure 4. Dependence of chloride ions concentration on zinc(II) ions distribution ratio for 4-pyridylketoximes (I = 4.0 mol/L (chloride/perchlorate solutions), a_w = 0.835, $[Zn^{2+}]$ = 0.010 mol/L, [oxime] = 0.10 mol/L).

of 4-pirydylketoximes. At the initial chloride ions concentration, the extraction degree of zinc cations (Zn^{2+}) by 1-(4-py-ridyl)tridecane-1-one oxime and 1-(4-pyridyl)pentadecane-1-one oxime increased to reach the maximum value for 1 mol/L Cl^- and after that slowly decreased (Figure 3).

This growing and decreasing dependence of chloride ions concentration on the logarithm of distribution coefficient of zinc(II) ions has been also observed by Cote and Jakubiak [2]. A similar growing and decreasing effect was also observed for chloride/perchlorate solutions at I = 4.0 mol/L (Figure 4). The zinc(II) ions distribution ratio initially increased to reach a maximum at 0.50 mol/L Cl^- (log D = 0.59 for 4PC12, 0.45 for 4PC10 and 0.29 for 4PC14). Then, for the concentration of chloride ions in the range of 0.5–1.0 mol/L, the log D value was constant and above 1.0 mol/L Cl^- it rapidly reduced to −0.02 for 4PC12, −0.67 for 4PC10 and −0.80 for 4PC14.

Figure 5 illustrates the effect of chloride ions concentration on zinc(II) ions distribution ratio for chloride/perchlorate solutions at I = 1.0 mol/L.

The extraction of zinc(II) ions by 4-pyridylketoximes increased with increasing chloride ions concentration to achieve 39% extraction efficiency (log D = −0.20) for 1-(4-pyridyl)tride-
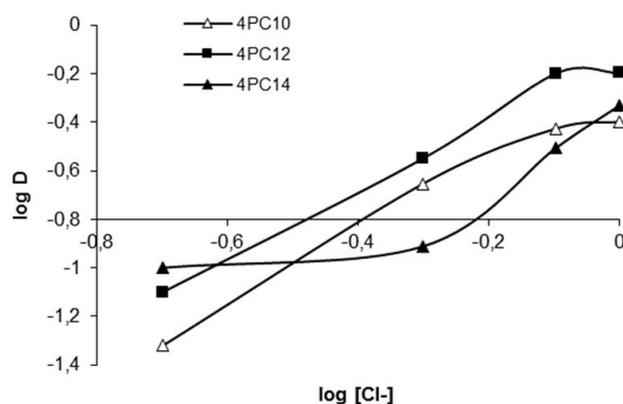
Figure 5. Dependence of chloride ions concentration on zinc(II) ions distribution ratio for 4-pyridylketoximes (I = 1.0 mol/L (chloride/perchlorate solutions), a_w = 0.966, $[Zn^{2+}]$ = 0.010 mol/L, [oxime] = 0.10 mol/L).
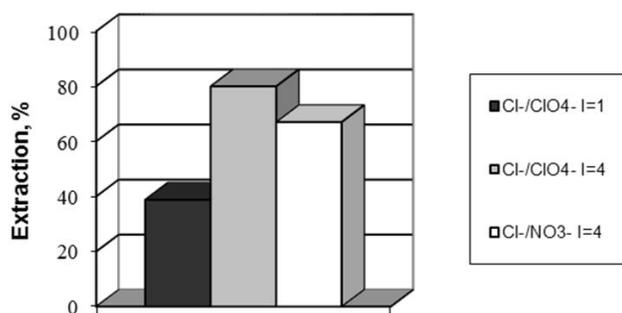
Figure 6. The influence of type of salts on extraction of zinc(II) ions from chloride solutions with 1-(4-pyridyl)tridecane-1-one oxime ([Cl⁻] = 1.0 M, [Zn²⁺] = 0.010 mol/L, [oxime] = 0.10 mol/L).

cane-1-one oxime and approx. 30% extraction efficiency (log D = –0.35) for oximes of 1-(4-pyridyl)undecane-1-one and 1-(4-pyridyl)pentadecane-1-one. The increase of extraction at low chloride ions concentration (below 1.0 mol/L) for chloride/perchlorate solutions was associated with the increase of the $ZnCl_2$ form, which was preferred in terms of forming complexes with pyridylketoximes. On the other hand, for solution containing concentrations of Cl⁻ higher than 1.0 mol/L, a decrease of the extraction efficiency with increasing of chloride ions concentration was observed. The effect was associated with the increased concentration of $ZnCl_3^-$ and $ZnCl_4^{2-}$ ions which, even at high concentration of $ZnCl_2$, limited the transportation of this metal to the organic phase [21].

In case of chloride/nitrate solutions with a low concentration of Cl⁻ ions and high concentration of NO₃⁻ ions, the dependence of zinc(II) ions extraction on the concentration of chloride ions was not apparent, therefore, at high concentration of NO₃⁻ ions it could be assumed that it is possible to coordinate zinc(II) salt ZnCl(NO₃).

The influence of ionic strength and type of salting-out agents on extraction of zinc(II) ions was also studied. The results for chloride ions concentration equal to 1.0 mol/L were shown in Figure 6. The extraction percent decreased with the decrease of ionic strength: for I = 1.0 mol/L the extraction was at 38.8% and for I = 4.0 mol/L it increased to 80% (compared to chloride/perchlorate systems). The change of salting-out agent from sodium perchlorate on sodium nitrate decreased the extraction from 80 to 67%.

3.5. Equilibrium extraction isotherms and stoichiometry of extracted complexes

Compositions of the extracted species were investigated. The slope analysis, based on the examination of the logarithmic variation of the distribution coefficient D vs. the concentration of ligand variable, is an effective method to obtain information regarding the number of ligands molecules in the extracted complex and also about the equilibrium constant K_{ex}.

The reaction between the solvating 4-pyridylketoximes (HL) and zinc(II) chloride for solutions with concentration of chloride ions = 2.0 mol/L can be described by equation:

$$Zn_w^{2+} + 2Cl_w^- + n\,HL_o = ZnCl_2(HL)_{n\,o} \qquad (2)$$
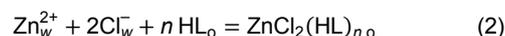
The equilibrium constant for the above reaction can be expressed, in terms of activities, as:

$$K_{ex} = \frac{[ZnCl_2 \cdot n\,HL]_o}{[Zn^{2+}]_w \cdot [Cl^-]_w^2 \cdot [L]_o^n} \qquad (3)$$

The following equation describes zinc speciation in the aqueous solutions:

$$[Zn]_T = [Zn^{2+}] + [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}] \qquad (4)$$

The formation constant for the above complexes is defined as:

Table 5. The slope as a results of examination of logarithmic plots of distribution coefficient of zinc(II) versus oxime equilibrium concentrations.

Oximes	Composition of aqueous phase	Slope	Metal:Ligand
4PC10	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/nitrate solution	1.44 (R^2 = 0.996) 2.19* (R^2 = 0.996)	1:1 1:2
	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/perchlorate solution	1.99 (R^2 = 0.989)	1:2
	1 mol/L Cl⁻, I = 1 mol/L, a_w = 0.961 chloride/perchlorate solution	1.28 (R^2 = 0.995)	1:1
4PC12	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/nitrate solution	1.17 (R^2 = 0.990)	1:1
	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/perchlorate solution	1.99 (R^2 = 0.999) 2.79* (R^2 = 0.983)	1:2 1:3
	1 mol/L Cl⁻, I = 1 mol/L, a_w = 0.961 chloride/perchlorate solution	1.92 (R^2 = 0.996)	1:2
4PC14	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/nitrate solution	1.38 (R^2 = 0.992)	1:1
	2 mol/L Cl⁻, I = 4 mol/L, a_w = 0.823 chloride/perchlorate solution	2.0 (R^2 = 0.993)	1:2
	1 mol/L Cl⁻, I = 1 mol/L, a_w = 0.961 chloride/perchlorate solution	1.29 (R^2 = 0.998)	1:1

* The slope for oxime concentration above 0.05 mol/L.

$$\beta_n = \frac{[ZnCl_n^{2-n}]}{[Zn^{2+}] \cdot [Cl^-]^n} \qquad (5)$$

When n varies from 1 to 4.

By substituting Eq. (5) to Eq. (4), it becomes:

$$[Zn]_T = [Zn^{2+}] + \left(1 + \sum \beta_n [Cl^-]^n\right) \qquad (6)$$

The substitution of Eq. (6) to Eq. (3) and considering the definition of D gives:

$$K_{ex}[Cl^-]^2 \cdot \left(1 + \sum \beta_n [Cl^-]^n\right) = \frac{D}{[HL]_0^n} \qquad (7)$$

Equation (7) can be rewritten as:

$$\log D = \log K_{ex} + n \log[HL] \qquad (8)$$

Where K_{ex} is an effective extraction constant defined as:

$$K_{ex} = k_{ex}[Cl^-]^2 \cdot \left(1 + \sum \beta_n [Cl^-]^n\right) \qquad (9)$$

Using this analysis, the extraction mechanism was graphically investigated by plotting $\log D$ as a function of $\log [HL]$ in the organic phase and the slopes were shown in Table 5.

For chloride/nitrate solutions ($I = 4.0$ mol/L; 2.0 mol/L Cl^-; 2.0 mol/L NO_3^-) 4-pyridylketoximes have a slope near 1 (for oximes 4PC10, 4PC12 and 4PC14 the slopes were 1.44, 1.17 and 1.38, respectively), which suggests that one molecule of the 4-pyridylketoxime coordinates one cation of zinc(II).

For chloride/perchlorate solutions ($I = 4.0$ mol/L; 2.0 mol/L Cl^-; 2.0 mol/L ClO_4^-) the slopes for oximes 4PC10 and 4PC14 are close to 2 (metal:ligand = 1:2). A similar slope was observed for oxime 4PC12, however the increase of the ligand concentration above 0.05 mol/L changed the slope from 1.99 to 2.80, which suggests the formation of a 1:3 (metal:ligand) complex.

The examination of the logarithmic plots of distribution coefficient of zinc(II) ions versus oximes equilibrium concentration was also carried out for chloride/perchlorate solutions with $I = 1.0$ mol/L (1.0 mol/L Cl^-). For 4PC12, the slope was close 2, similar to solutions with $I = 4.0$ mol/L. However, the slopes obtained for the remaining 4-pyridylketoximes were smaller: 1.28 for 4PC10 and 1.29 for 4PC14.

3.6. Extraction capacity of oximes

The loading test of zinc(II) ions by all examined oximes was also conducted. The relation between the molar ratio of
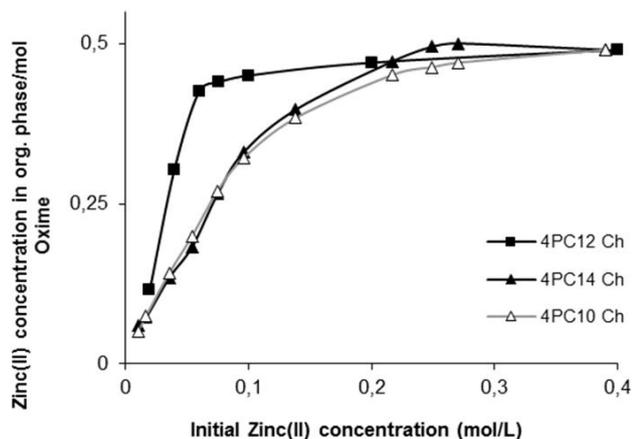
Figure 7. Loading isotherms of zinc(II) ions from chloride-/nitrate solutions ([Cl^-] = 2.0 mol/L, [oxime] = 0.10 mol/L).
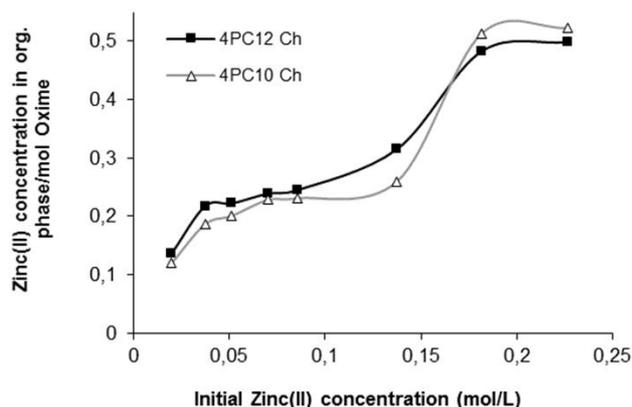
Figure 8. Loading isotherms of zinc(II) ions from chloride/perchlorate solutions ([Cl^-] = 2.0 mol/L, [oxime] = 0.10 mol/L).

the zinc(II) ions to the extractant in the chloroform solutions and the initial zinc(II) ions concentration in the aqueous phase in chloride/nitrate and chloride/perchlorate solutions with $I = 4.0$ mol/L and $a_w = 0.835$ were shown on Figure 7 and 8, respectively.

The obtained results suggest that the molar ratio of zinc cations to 4-pyridylketoximes was 1:2 in both studied chloride/nitrate and chloride/perchlorate solutions. However, in chloride/nitrate solutions 1-(4-pyridyl)tridecane-1-one oxime achieved maximum loading much faster than the rest of the tested oximes. The decrease of ionic strength to $I = 1.0$ mol/L did not change the zinc(II):oxime relation and for this system it was also at 0.5.

3.7. Stripping process

Zinc(II) could be effectively stripped from the organic solution by water, 0.10 mol/L NH_4OH and 0.10 mol/L HCl. Regardless of the construction of ligand, the extraction and type of re-extractant, the stripping was almost 100% (Table 6).

Hydrochloric acid seems to be good stripping solution, however it causes a slight decrease in the percentage of successive stages of extraction with oximes of 1-(4-pyridyl)undecane-1-one or 1-(4-pyridyl)pentadecane-1-one. The reduction of extraction was associated with the ability to transfer the HCl to the organic phase and the blocking of the coordination center. Ammonium solutions would make a good choice for the

Table 6. Results of zinc(II) ions stripping from the organic phase.

Oxime	Composition of aqueous phase	Re-extraction %
4PC10	0.10 mol/L HCl	100
	0.10 mol/L NH₄OH	90
	Water	97
	0.10 mol/L HCl	98
4PC12	0.10 mol/L NH₄OH	95
	Water	100
	0.10 mol/L HCl	100
4PC14	0.10 mol/L NH₄OH	92
	Water	98

Table 7. Results of zinc(II) ions multi-extraction-stripping processes.

Stage of extraction	Extraction percent %	Re-extraction %
I	80	98
II	83	100
III	79	97
IV	80	99

stripping agent, since they did not cause problems with turbidity and phase separation, however ammonia solutions cause problems in the further analysis, especially with EDTA determination of metal concentration. Water is the best stripping solution. After two stages of stripping, the zinc(II) ions were completely removed from the loaded solutions. Moreover, there were no problems with emulsions and precipitation, both phases separate very fast.

3.8. Investigations on the re-use of extractant

The 1-(4-pyridyl)tridecane-1-one oxime did not lose the extraction ability after re-extraction of metal ions with water. Even after repeated extraction-stripping processes, the metal ions were removed from the aqueous phase in an amount comparable to the initial results (Table 7).

3.9. Separation of zinc(II) ions from solutions containing cadmium(II) and copper(II) ions

The recovery and separation of different metals ions, including Zn(II), Cd(II) and Cu(II), is a common problem in hydrometallurgy. It is important to investigate whether cadmium(II) ions in the presence of zinc(II) ions or other metal ions were not co-extracted. The 2-pyridylketoximes were used earlier for the separation of copper(II) ions from solutions containing copper(II), zinc(II) and cadmium(II) ions, but Zn(II) and Cd(II) were not removed from aqueous phases [15,16]. Another study [14] demonstrated that 4-pyridylketoximes did not extract cadmium(II) from the chloride solution. Based on these reports, the selective study of zinc(II) removal from a solution containing cadmium(II) and copper(II) ions was proposed.

In this study the extraction of zinc(II) ions in the presence of cadmium(II) and copper(II) ions using the 1-(4-pyridyl)tridecane-1-one oxime dissolved in chloroform as an extractant was studied. The research was carried out for chloride/nitrate solutions with 2.0 mol/L Cl⁻. The study of the removal of Zn(II) and Cd(II) suggested that zinc(II) ions were extracted from multi-elemental solutions in a comparable amount to that obtained during the basic research (about 80% extraction). Additionally, no co-extraction of cadmium(II) ions (0% extraction) was observed. Unfortunately, when the aqueous phase also contained copper(II) ions, 1-(4-pyridyl)tridecane-1-one oxime transferred copper(II) ions to the organic phase as easily as zinc(II) ions and Cu(II) was removed in 100%. Therefore, the recovery of zinc(II) ions from a solution containing copper(II) ions would require the removal of Cu^{2+} during an earlier stage of the cleaning solution using 4-pyridylketoxime in toluene with 10% addition of decan-1-ol solution or other selective extractant. Selective recovery of zinc(II) ions from aqueous media which also contain copper(II) is not possible.

4. Conclusions

The basic studies regarding the recovery of zinc(II) ions from chloride media suggest that the extraction of zinc(II) ions by 4-pyridylketoximes was rapid and optimal contact time was found to be 30 min. The change of pH did not affect the percentage of extraction however pH below 2 may cause precipitation or emulsion formation.

The obtained results show that the concentration of chloride ions influenced the extraction degree of zinc(II) ions. For example, the extraction degree of zinc(II) chloride from chloride/nitrate solutions (with I = 4.0 mol/L at initial chloride ions concentration) by 1-(4-pyridyl)tridecane-1-one oxime and 1-(4-pyridyl)pentadecan-1-one oxime increased to reach a maximum for 1.0 mol/L Cl⁻ and after that slowly decreased. The growing and decreasing extraction is associated with the changing concentration of $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$. The decreasing effect on zinc(II) ions extraction was also observed when ionic strength was changed from 4.0 mol/L on 1.0 mol/L and when sodium nitrate was used as the salting-out agent.

Based on the graphical analysis, the composition of the complexes in chloride/nitrate and chloride perchlorate solutions was determined. In the first system, the ligand:metal molar ratio was at 1:1. The presence of perchlorate ions at I = 4.0 mol/L allowed to form mostly 1:2 complexes. Change of ionic strength affected the composition of the complex, and the analysis carried out for 1-(4-pyridyl)undecane-1-one oxime and 1-(4-pyridyl)pentadecane-1-one oxime showed the presence of the complex 1:1 in solution while for 1-(4-pyridyl)-tridecane-1-one oxime the graphical analysis suggested the presence of the 1:2 complex.

The loading test of zinc(II) ions by all examined oximes was also conducted and showed the maximum about 0.50 mol Zn/mol ligand.

Zinc(II) ions could be effectively stripped by water, 0.10 mol/L HCl and 0.10 mol/L NH_4OH from the loaded organic phase. However, water seems to be the best stripping reagent (after repeated extraction-stripping process, the metal ions were removed from aqueous phase in an amount comparable to the initial results).

The 4-pyridylketoximes could be used as selective extractants of zinc(II) chloride from solutions containing cadmium(II) ions. Copper(II) ions was transferred with 1-(4-pyridyl)tridecane-1-one oxime to the organic phase as easily as zinc(II) ions and even selective recovery was not possible.

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