INTRODUCTION

Zinc is an important base metal involved in various applications in metallurgical, chemical and textile industries. It is mainly recovered from primary sulphide concentrates. A part of zinc is also recovered from different secondary resources such as zinc ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge etc. Wastewater effluents, solid industrial waste and sewage are considered as the main pathways of zinc to aquatic environment. With rising environmental awareness, the presence of heavy metals, in nature is severely controlled. Although zinc in micro amount is an essential oligo-element for a healthy body, zinc...
excess can be harmful, and causes zinc toxicity\(^5\). Therefore, zinc is listed in dangerous substance, and contamination lists proposed respectively, by European Union Directive and the United States Environmental Protection Agency (USEPA)\(^6\). The World Health Organisation (WHO) and USEPA recommend respectively, 3.0 and 5.0 \(\text{mg/L}\) as maximal acceptable concentrations of zinc in drinking water\(^6\). The effluent standards are set at 2 \(\text{mg/L}\), and 2.5 \(\text{mg/g}\), respectively for wastewater\(^4\), and solid waste disposal\(^6\). Reducing the discharge of this element into surface water becomes crucial operation\(^4,7\). For compliance with strict environmental regulation, developing process for the recovery of zinc from leach solutions, spent solution and effluents becomes increasingly important\(^8\). Several methods are used to achieve this purposes such as chemical precipitation, liquid–liquid extraction, ion exchange, and adsorption. Among these methods, liquid-liquid extraction is the most promising process for the separation and recovery of metals from the complex and low metallic containing solutions, for being one of the most economical and practical processes\(^2,9,10\). Some conventional treatment techniques are less efficient, especially when zinc concentration effluent is relatively low\(^4\).

The extraction of zinc is often carried out using high molecular weight amines and/or phosphoric, \((\text{RO})_2\text{P}0_2\text{H}\), phosphonic, \((\text{RO})(\text{R})\text{P}0_2\text{H}\), and phosphinic, \((\text{R})\text{P}0_2\text{H}\), acid extractants, from sulfuric and chloride acids media\(^2,8,11-19\). The advantage of these mixing systems is due to the ability of used reagents to combine complexation phenomena and ion exchange processes. Some conventional treatment techniques are less efficient, especially when zinc concentration effluents is relatively low\(^4\).

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Recently, there has been an increasing interest in the development of chelating ion exchangers with the amino acid groups to improve the extractability and selectivity of heavy metal ions\(^19\). Among the chelating ligands, quinoxalines have found extensive applications in coordination chemistry due to ease of preparation, and as they can form stable complexes with most transition metal ions\(^21,22,38-39\).

To remove zinc more efficiently and economically requires more extensive information on the interaction of this element, with various extractant ligands, and inorganic anions. HNO\(_3\) is suitable for a digestion of concentrated organic samples. The aim of the present study is to examine the extraction of zinc in NO\(_3\) medium, with 3-methyl-2(1H) quinoxalinethione which is a bifunctional extractant groups. The advantage of this process is that it can combine complexing phenomena, ion-pair formation, and ion exchange reactions.

**EXPERIMENTAL**

**Reagents and synthesis of 3-methyl-2 (1H)-quinoxalinethione**

A 0.1 \(M\) HNO\(_3\) stock solution of \(10^{-3} M\) Zn (II) is obtained by dissolution of known amount of Highly pure Zinc Nitrate Hexahydrate \([\text{Zn(NO}_3\text{)}_2\text{.6H}_2\text{O}], 99.999 \text{ wt%}\) in adequate volume of nitric acid (HNO\(_3\)). A solution of synthesized extractant is prepared with dissolution of 0.011 \(M\) of 3-methyl-2 (1H) quinoxalinethione \((\text{C}_9\text{H}_8\text{N}_2\text{S})\) in toluene \((\text{C}_7\text{H}_8)\). All reagents are of analytical grade and used without further purification.

The synthesized of 3-methyl-2 (1H)-quinoxalinethione \([\text{LH}]\) is well described in literature. Briefly, the condensation of o-phenylenediamine and ethyl pyruvate in distilled water acidified (by sulphuric acid) for one hour at room temperature, results in the formation of 1: 3-methylquinoxalin-2 (1H), which is purified by recrystallization. Reaction of obtained compound with \(\text{P}_2\text{S}_5\) in refluxing pyridine for four hours gives 2: 3-methyl-2 (1H)-quinoxalinethione \((\text{Rdt} : 75\%)\). (Figure 1.).

**Procedure**

The organic and aqueous solutions were equilibrated in 20 \(mL\) separator funnel with an organic/aqueous ratio of 1:1 \((5mL/5mL)\) which is shaken vigorously for 15 \(min\). Preliminary tests have shown that equilibrium of extraction is reached in less than 5 \(min\). The starting pH of the aqueous phase, is adjusted by addition of drops of LiOH/HClO\(_4\) or KOH/HNO\(_3\), and measured before and after extraction test. After equilibration, the separator funnel is left standing for at least 10 \(min\) for completing phase separation. The aqueous zinc is then analyzed using Zincon (2-carboxy-2'-hydroxy-
5'-sulfoformazylbenzene) spectrophotometry method\textsuperscript{25, 26}. The extraction experiments are carried out in duplicate at room temperature, as a function of pH, and concentrations of nitrate ion and extractant designated thereafter as C\textsubscript{NO\textsubscript{3}} and C\textsubscript{LH}, respectively. The zinc (II) concentration in the organic phase is obtained by mass balance. The distribution ratio, D, is calculated from the ratio of the equilibrium concentration of Zn(II) in the organic phase to that in the aqueous phase.

The effect of the initial zinc concentration (C\textsubscript{Zn}) on the extraction was studied in the range 0.001M– 0.2 M (Figure 2). It was observed that the LH gives a better extraction for concentrations lower than 10\textsuperscript{-3}M Zn (II).

### RESULTS AND DISCUSSION

**Effect of equilibrium pH**

The variation of logD versus pH obtained at C\textsubscript{NO\textsubscript{3}} = 10\textsuperscript{-2} M, for various analytical concentrations, C\textsubscript{LH}, of chelatant are given in Figure 3. Similar variations with “S” shape are reported for the extraction of zinc and other divalent metals with some acidic extractants\textsuperscript{27}. Distinct pH regions with different slopes characterize the various extracted species, and suggest the change in extraction mechanism.

As observed, extraction mechanism is less dependent on medium acidity for pH < 3. This process is ion-pair formation involving protonated amine group\textsuperscript{25}.

For pH > 3, the extraction mechanism is typical of ion exchange. As a result, logD increases with pH to reach a maximum at pH\textsubscript{max} and then decreases as pH continues to rise. Optimum pH\textsubscript{max} is found at 4.7, in all explored C\textsubscript{LH} conditions.

When pH becomes higher than pH\textsubscript{max} (4.7) the functional groups with strongly acidic cation exchanger “sulphonate -SO\textsubscript{3}H” reach its maximum sorption capacity\textsuperscript{26}.

On the other hand the ternary amine in position 4 is protonated and sites of bonding to metal ions are limited en ternary amine in position 2 so the extraction is decreased\textsuperscript{26}.

At pH 5.6 and higher, zinc seems to exhibit a typical hydroxylated species extraction behavior\textsuperscript{26}. Similar trend in removal efficiency with pH is reported on the extraction of Zn(II) and analogous divalent metals with organophosphorus extractants\textsuperscript{12, 27}. The hydrolysis equilibrium can be expressed as:

\[
\text{Zn}^{2+} + h \text{H}_2\text{O} \leftrightarrow \text{Zn(OH)}_{(2-h)}^{(2-h)^+} + h \text{H}^+ \quad \ldots(3)
\]

![Fig. 1: Reaction of condensation of o-phenylenediamine and 1,2-diketones and sulfidation of the 3-methyl quinoxalin-2-thione](#)

![Fig. 2: Variations of logD=f(C\textsubscript{Zn}) obtained at C\textsubscript{NO\textsubscript{3}}= 10\textsuperscript{-3} M, for analytical extractant (HL) concentrations of 0.002 and 0.01M](#)
If \( D_0 \) designate the particular value of distribution coefficient in the absence of hydrolysis phenomenon, we obtain

\[
y = \frac{D_0 - D}{D} = \sum K_H \left[ H^+ \right]^h
\]  

\( K_H \) is the apparent hydrolysis equilibrium constant.

The computation of \( \log D_0 \) is performed on the basis of corresponding linear equation of \( \log D = f(\text{pH}) \) (Figure 3.), obtained at \( C_{HL} = 0.01 \text{M} \) and \( \text{pH} > 5.6 \). Figure 4 shows that \( \log y = f(\text{pH}) \) variations are linear with slope \( (h) \) varying in the range : 1.3 – 1.4. As a result for \( \text{pH} \) range: 5.6-6, the both first and second hydrolysis reactions are involved, in these conditions.

Taking into consideration the molar fraction \( (x) \) of \( Zn(OH)^+ \) specie, the overall hydrolysis equilibrium could be written as

\[
\begin{align*}
\text{Zn}^{2+} + (2-x)\text{H}_2\text{O} \leftrightarrow Zn(OH)_{2aq}^2+ + 2H^+, \quad K_{HOV}, \quad 1 \leq h \leq 2
\end{align*}
\]

\( K_{HOV} \) is the overall hydrolysis constant. Based on the experimental results (Figure 4-2), we obtain \( \log K_{HOV} = -6.55 \) and \( x = 0.61 \). This indicates that \( Zn(OH)^+ \) and \( Zn(OH)_{2aq}^2+ \) are the hydrolyzed species formed in this case, and their molar fraction are 61% and 39%, respectively.

**Effect of extractant concentration**

As shown from \( \log D = f(\text{pH}) \) study, the extraction of \( \text{Zn(II)} \) with 3-methyl-2 (1H)-

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**Fig. 3:** Variations of \( \log D = f(\text{pH}) \) obtained at \( C_{NO_3} = 10^{-2} \text{M} \), for analytical extractant \( [HL] \) concentrations of 0.002, 0.005, 0.008 and 0.01M

**Fig. 4:** Variations of \( \log \left( \frac{D_0 - D}{D} \right) = f(\text{pH}) \) obtained at \( C_{HL} = 10^{-2} \text{M} \), for extractant \( [HL] \) concentrations of 0.002, 0.006, 0.009 and 0.01M
quinoxalinethione is a complex process involving, more than one extraction reaction. In order to have a better understanding of the extraction mechanism, further information is required in this case. For this reason, experimental analysis of the logarithmic variation of D with C_HL is undertaken at pH values ranging from 2 to 6.0 (Figure 5). As found, straight lines with slopes close to 1.5 and 1.1 are obtained in the pH ranges of 1.3 – 5.0 and 5.6 – 5.9, respectively. So, the stoichiometry coefficient, \( \beta = \frac{\partial \log D}{\partial \log [C_{HL}]} \), is not integer as might be expected from theoretical single reaction. Thus, for pH < 5 the extraction of zinc in nitrate medium, by 3-methyl-quinoxaline-2-thione, results in a combination of at least two predominant extracted complexes with 1 (\( l = 1 \)) and 2 (\( l = 2 \)) extractant ligands. While for pH ≤ 5.6 the 1:1 metal-ligand complex is the prevailing extracted species. Previous studies report that the metal: extractant ligand ratio of 1:1, and 1:2 is obtained for the extraction mechanisms of Zn(II) with amine and/or organophosphorus chelatants^{15,28}.

**Effect of nitrate concentration (C_{NO3})**

The effect of nitrate anion added as NaNO\(_3\) is examined in 0.01M nitric acid solution (pH=2), for C_HL=0.01M and C_{NO3} ranging from 0.01 to 0.2M. Obtained results are reported in Figure 6.

As it can be observed extraction of zinc by 3-methyl-2 (1H)-quinoxaline-2-thione increases with increasing C_{NO3}, and reaches a maximum of 97% at C_{NO3}=0.07M. The plots of logD=f(log C_{NO3}) (Figure 5) exhibits straight lines with different slopes, indicating that extraction reaction involves the formation of complexes with various Zn(II) : NO\(_3^−\) molar ratio, as discussed thereafter.

**Extraction reactions of Zn\(^{2+}\) with 3-methylquinoxaline-2-thione.**

It has been reported from previous study that zinc is extracted into chloroform with shift base extractants as both uncharged chelate complexes, and ion-pairs of charged species with a counter anion in aqueous solution^{27}. Taking into account the protonation of amino group at pH <3^{20,30}, and neglecting the complexing effect of NO\(_3^−\)^{31}, the
The extraction reaction of the predominant Zn\(^{2+}\) species by 3-methyl-quinoxaline-2-thione symbolized as LH in following, comibines-pair formation and ionic exchange mechanisms. These reactions are expressed by the general equations:

\[
\text{Zn}^{2+} + (\text{LH})_n\text{NO}_3^-(\text{aq}) \leftrightarrow \text{Zn(LH)}_n\text{NO}_3^+(\text{aq}), \quad n = 0, 1, 2, \ldots
\]

\[
\text{Zn}^{2+} + \text{LH} + \text{H}^+ \leftrightarrow \text{Zn(LH)}_n\text{H}_m\text{NO}_3^+(\text{aq}), \quad n = 0, 1, 2, \ldots \text{ for } \text{pH} < 3
\]

In the above equations, the online entities refer to organic phase and \(n\) = 0; 1; 2; etc. The symbol \(\text{H}_n\) stands both for hydrogen atoms \((n<0)\) and for OH group \((n>0)\).

The corresponding D expression being

\[
\frac{[\text{Zn}]}{[\text{Zn}^{2+}]} \quad \text{(10)} \quad \text{or} \quad \left[\frac{\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+}{\text{Zn}^{2+}}\right] = \left[\frac{\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+}{\text{Zn}^{2+}}\right]
\]

For ion-pair equilibrium (8), the extraction constants:

\[
K_{nl} = \frac{[\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+]}{[\text{Zn}^{2+}]^{n}[\text{H}^+]^n} \quad \text{(11)}
\]

Equation (10) can be rearranged in the form

\[
D = K_{nl} \left[\frac{\text{LH}_2^+}{\text{NO}_3^-}\right]^{n} \quad \text{(12)}
\]

Assuming, in first approximation, that

\[
\frac{[\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+]}{[\text{Zn}^{2+}]} = C_{\text{LH}} \quad \text{and} \quad \frac{[\text{NO}_3^-]}{[\text{NO}_3^-]} = C_{\text{NO}_3^-}
\]

we obtain

\[
\log D = \log K_{nl} + n\log C_{\text{LH}} + n\log C_{\text{NO}_3^-} \quad \text{(13)}
\]

For ionic exchange mechanism (9) the extraction constant, \(K_n\), is

\[
K_n = \frac{[\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+]}{[\text{Zn}^{2+}]^{n}[\text{H}^+]^n} \quad \text{(14)}
\]

and \(D\) is given by:

\[
D = \frac{[\text{Zn}(\text{LH})_n\text{H}_m\text{NO}_3^+]}{[\text{Zn}^{2+}]^{n}[\text{H}^+]^n} \quad \text{(15)}
\]

Taking into account the approximations given above, \(\log D\) can be expressed as:

\[
\log D = \log K_{nl} + n\log C_{\text{LH}} + n\log C_{\text{NO}_3^-} \quad \text{(16)}
\]

It appears that the distribution coefficient must be obtained in all cases, according to the general equation:

\[
\log D = \log K_{nl} + n\log C_{\text{LH}} + m\log C_{\text{NO}_3^-} + \log C_{\text{NO}_3^-} \quad \text{(17)}
\]

Where \(m = l\) and \(n = 0\) for \(\text{pH} < 3\), and \(m = 0\) and \(n = 0\) in the \(\text{pH}\) range of \(3 \leq \text{pH} \leq 5.6\).

At given \(C_{\text{NO}_3^-}\) and \(\text{pH}\), equation (17) can be written as:

\[
\log D = \log A + \log C_{\text{HL}} \quad \text{(18)}
\]

with

\[
\log D = \log A + \log C_{\text{HL}} \quad \text{(19)}
\]

\[\begin{align*}
\text{y} & = 0.021x + 2.3; \quad R^2 = 0.999\quad (\text{pH} \leq 3) \\
\text{y} & = 0.986x - 0.393; \quad R^2 = 0.987\quad (3 \leq \text{pH} \leq 4.2)
\end{align*}\]
 Whereas at fixed $C_{HL}$ and pH, the expression of logD becomes

$$\log D = \log B + m\log C_{HNO_3}$$  \hspace{1cm} (20)

with

$$\frac{\delta \log D}{\delta \log C_{HL}} = l$$  \hspace{1cm} (22)

$$\frac{\delta \log D}{\delta \log C_{NO_3}} = m$$  \hspace{1cm} (23)

$$\frac{\delta \log D}{\delta \log A} = n = \frac{\delta \log A}{\delta \log pH}$$  \hspace{1cm} (24),

The exploitation of the distribution data on the basis of the general extraction equilibrium allows us to define the nature of the extracted complexes formed according to:

$$l = \log C + \log K_{HL}$$  \hspace{1cm} (22)

$$m = 3\log C + \log K_{HNO_3}$$  \hspace{1cm} (23)

$$n = \log C + \log K_{B}$$  \hspace{1cm} (24).

From results obtained at pH=2,$\log C_{HL}$=-2, and $C_{NO_3} \leq 0.07M$ (Figure 6), the straight line is of a slope 1.4 which is consistent with that of logD=f(logC) (Figure 5). Obtained at pH\(\geq 5\), showing $l=1.5$ which is comparable to $m=1.4$. The origin ordinate of obtained straight line which corresponds, in these conditions, to ion-pair mechanism, leads to $\log K_{01.5}=7.42$.

In addition, we have deduced from the experimental data logD=f(logC$_{HL}$) (Figure 5), obtained at different pH values the variations of log A=f(pH) at $C_{NO_3}=10^{-2}M$ (Figure 7). Straight lines having slopes of 0 and 1 are obtained respectively, at pH < 3 and 3 \(\leq\) pH \(\leq 5\). These results are in agreement with those of Figure 2, indicating that Zn(II) is extracted with 3-methyl-quinoxaline-2-thione, essentially, by ion-pair formation in acidic medium (pH < 3), and by 1H+ exchange reaction, in low acidic medium (3 \(\leq\) pH \(\leq 5\)).

Accordingly, both ion-pair and ion exchange extracted complexes, involve 50% of $ZnL^+$ and, respectively. Similar
complexes with 1:1 or 1:2 divalent metal-schiff base ligand stoichiometry are reported in literature 29-30, 32-34.

CONCLUSION

Extraction of zinc from nitrate medium is carried out using 3-methyl-2 (1H)-quinoxalinethione in toluene. The extraction equilibrium of Zn(II) is examined as a function of pH, nitrate and chelate concentrations. The stoichiometry and the stability constants of the extracted Zn²⁺ species is postulated based on slope analysis method. Obtained results show that the extraction reaction involves both ion-pair formation and 1H⁺ exchange mechanism. The stoichiometry of the prevailing complexes are found to be 1:1 and 1:2 metal-ligand ratios, in all cases. The molar fraction of these complexes is evaluated. It is found that extracted species include 50% of each of identified complexes in all explored conditions. The formation of hydroxylated species is also considered. The formation of Zn(OH)⁺ and Zn(OH)₂aq is shown to take place for pH >5.6, their molar fraction are 61% and 39%, respectively. In addition, extraction of zinc by 3-methyl-2 (1H)-quinoxaline-2-thione increases with increasing C₃NO₃⁻, and reaches a maximum of 97% at C₃NO₃⁻ = 0.07 M / pH=2.

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