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Liquid-liquid Extraction of Zinc by 3-methyl-quinoxaline-2-thione from Nitrate Medium

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ABSTRACT

The extraction of zinc with 3-methyl-2 (1H)-quinoxalinethione $(\overline{LH})$, is investigated in nitrate solution as a function of pHrange 2-6, and analytical concentrations of NO_3^- anions (C_{NO_3}) and extractant (C_{LH}). The extraction mechanism with $\overline{\mathrm{LH}}$, is determined on the basis of the variation of the distribution coefficient D with pH, C_{NO_3} and C_{LH} . As a result, the partition equilibrium involves complexing phenomenon, ion-pair formation, and 1H$^+$ exchange reaction. The overall extraction constants are logK$_{01.5}$ = 5.1, and logK$_{11.5}$ = -0.6. The extraction complexes are found to be $\overline{\mathrm{Zn(LH_2)}_l\mathrm{(NO_3)}_{l+2}}$, and $\overline{\mathrm{Zn(L)\ (LH)}_{l\text{-}1}\mathrm{(NO_3)}}$ with l = 1 or 2. The hydrolysis reaction of Zn(II) is evaluated and it is found that it results in the formation of $\mathrm{Zn(OH)}^+$ and $\mathrm{Zn(OH)}_{2aq}$ species, at pH >5.6. Zinc shows maximum percent extraction (75%) with the pH 4.7 at low organic ligand concentration (0.01M).

Key words: Liquid-liquid Extraction, zinc, 3-methyl-quinoxaline-2-thione, nitrate medium, pH range: 2-6.

INTRODUCTION

Zinc is an important base metal involved in various applications in metallurgical, chemical and textile industries[1-5]. 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[7, 37].Wastewater effluents, solid industrial waste and sewage are considered as the main pathways of zinc to aquatic environment[3].With rising environmental awareness, the presence of heavy metals, in nature is severely controlled[6]. 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 indangerous 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 mg/L as maximal acceptable concentrations of zinc in drinking water[6]. The effluent standards are set at 2 mg/L, and 2.5 mg/g, respectively for wastewater[4], andsolid 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 purposesuch 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 treatmenttechniques are less efficient, especially when zincconcentration effluentis relatively low[4].

The extraction of zinc is often carried out using high molecular weight amines and/or phosphoric, $(RO)_2P0_2H$,phosphonic, $(RO)(R)P0_2H$, and phosphinic, $(R)_2P0_2H$, acid extractants, from sulfuric and chloride acids media[2,8, 11-19].The advantage of these mixing systemsis due to ability of used reagents to combine complexation phenomenonand ion exchange process.

Recently, there has beenan increasing interest in the development ofchelating ion exchangers with the aminoacid groups to improve the extractability and selectivity of heavy metal ions[19]. Among the chelating ligands, quinoxalines have foundextensive applications in coordination chemistrydue 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) quinoxaline-thione which is a bifunctionalextanctant groups.The advantage of this process is that 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 ZincNitrate Hexahydrate[$(Zn(NO_3)_2,6H_2O)$, 99.999*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) quinoxaline-thione($C_9H_8N_2S$) in toluene(C_7H_8). All reagents are of analytical grade and used without further purification.

The syhthesized of 3-methyl-2 (1H)-quinoxalinethione$\left(\overline{LH}\right)$is well described in literature[23, 24].Briefly, the condensation of o-phenylenediamine and ethyl pyruvate in distilled water acidified (by sulphuric acid) for one hourat room temperature, results in the formation of 1: 3-méthylquinoxalin-2 (1H), which is purified by re-crystallization.Reaction of obtained compound with P_2S_5in refluxing pyridine for four hours gives 2: 3-methyl-2 (1H)-quinoxalinethione(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 (5*ml* organic solution and 5*ml* aqueous solution) 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 phases,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[25, 26].Theextraction experiments are carried out in duplicate at room temperature, as a function of pH, and concentrations of nitrate ionand extractantdesignated thereafteras C_{NO3} and C_{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 one in the aqueous phase.

The effect of the initial zinc concentration (C_{Zn}) on the extraction was studied in the range 0.001*M*– 0.2 *M* (Figure2). It was observed that the LH gives a better extraction for concentrations lower than 10^{-3}*M* Zn (II).

RESULTS AND DISCUSSION

Effect of equilibrium pH

The variation of logD versus pH obtained at C_{NO3}= 10^{-2} *M*, for various analytical concentrations, C_{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[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[20].

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

When pH becomes higher than pHmax (4.7)the functional groups with strongly acidic cation exchanger "sulphonate -SO3H" reach its maximum sorption capacity[20].

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[35].

At pH 5.6 and higher, zinc seems to exhibit a typical hydroxylated species extraction behavior[36]. Similar trend in removal efficiency with pH is reported on the extraction of Zn(II) and analogous divalent metals with organophosphorus extractants[12, 27]. The hydrolysis equilibrium can be expressed as:

$$Zn^{2+} + h\,H_2O \leftrightarrow Zn(OH)_h^{(2-h)+} + h\,H^+ \qquad ...(3)$$

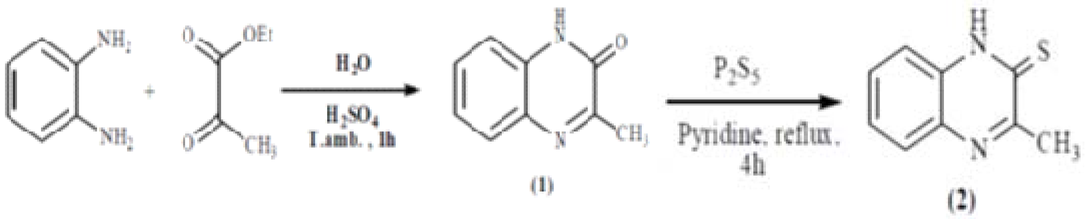

Fig. 1: Reaction of condensation of o-phenylenediamine and 1,2-diketones and sulfidation of the 3-methyl quinoxalin-2-thione $\left(\overline{HL}\right)$[22, 24]

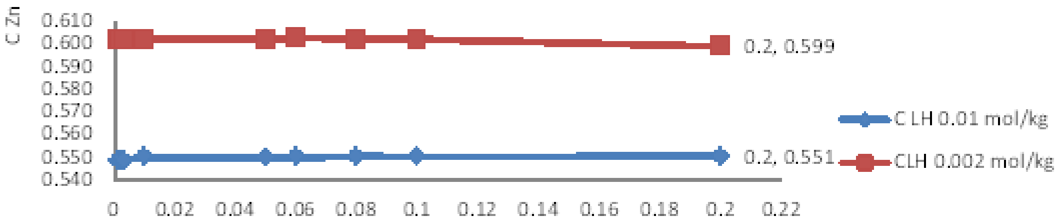

Fig. 2: Variations of logD=f(C_{Zn}) obtained at C_{NO3}= 10^{-2} M, for analytical extractant $\left(\overline{HL}\right)$ concentrations of 0,002 and 0,01M

If D_0 designate the particular value of distribution coefficient in the absence of hydrolysis phenomenon, we obtain

$$y = \frac{D_O - D}{D} = \sum_{h} K_H \left[H^+\right]^{-h} \qquad ...(4)$$

K_H is the apparent hydrolysis equilibrium constant.

The computation of $\log D_0$ is performed on the basis of corresponding linear equation of logD =f(pH) (Figure 3.), obtained at C_{LH} = 0.01M and pH >5.6. ***Figure 4*** shows that logy = f(pH) variations are linear with slope (*h*)varying in the range : 1.3 – 1.4. As a result for 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

$$x\left(Zn^{2+} + H_2O \leftrightarrow \ Zn(OH)^+ + H^+\right) \qquad (5)$$

$$(1\text{-}x)\left(Zn^{2+} + 2H_2O \leftrightarrow \ Zn(OH)_{2aq} + 2H^+\right) \qquad (6)$$

$$Zn^{2+} + (h = 2 - x)H_2O \leftrightarrow \ Zn(OH)_h^{(2-h)+} + hH^+, \quad K_{Hov}, \quad 1 \le h \le 2 \quad (7)$$

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

Effect of extractant concentration

As shown from logD=f(pH) study, the extraction of Zn(II) with 3-methyl-2 (1H)-

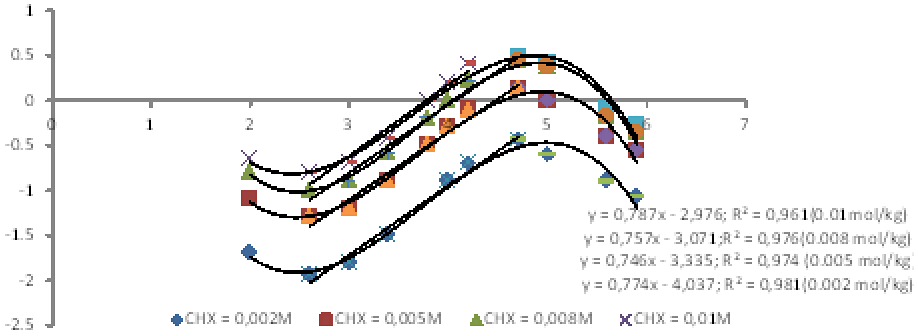

Fig.3: Variations of logD=f(pH) obtained at CNO_3= 10^{-2} M, for analytical extractant $\left(\overline{HL}\right)$concentrations of 0,002, 0,005, 0,008 and 0,01M

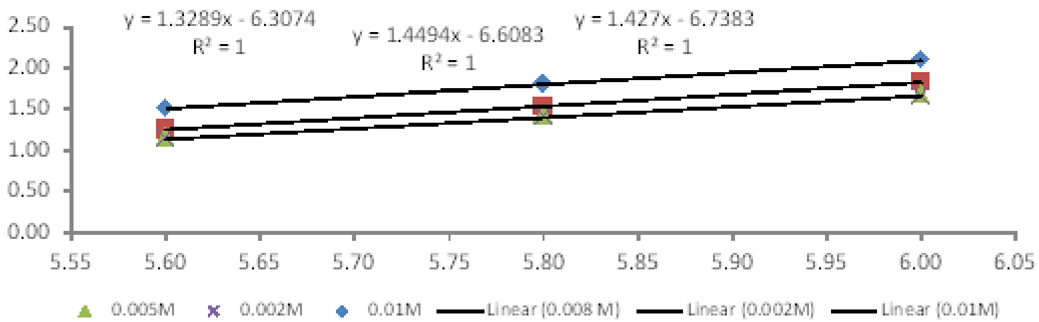

Fig. 4: Variations of log ($y = \frac{D_O - D}{D}$) = f(pH) obtained at C_{NO3}= 10^{-2} *M*, for extractan $\left(\overline{HL}\right)$ concentrations of 0,002, 0,006, 0,009 and 0,01*M*

quinoxalinethioneisa complex process involving, more than one extraction reaction. In order to have a better understanding of theextraction mechanism,further information is required in this case. For this reason, experimentalanalysis of the logarithmic variation of D with C_{LH}, is undertaken at pH valuesranging from2 to 6.0 (**Figure 5.).**As found,straight lines with slopesclose to 1.5 and 1.1are obtained in the pH ranges of 1.3 – 5.0 and 5.6 – 5.9, respectively.So, the stoichiometry coefficient, $l=\left(\frac{\partial \log D}{\partial \log(C_{LH})}\right)_{pH}$, 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 with1 (*l* =1) and 2 (*l* =2) extractant ligands. While for pH ≤ 5.6 the 1:1 metal-ligand complex is the prevailing extracted specie. 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/ ororganophosphoruschelatants[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_{LH}=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_{NO_3} , and reaches a maximum of 97% at C_{NO3}=0.07M. The plots of logD=f(log C_{NO_3}) (Figure 5) exhibits straight lineswith differentslopes, 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-methyl-quinoxaline-2-thione.

It has been reported from previous study that zinc is extracted into chloroform with shift base extractants asboth uncharged chelate complexes, and ion-pairs of charged species with a counter anionin 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

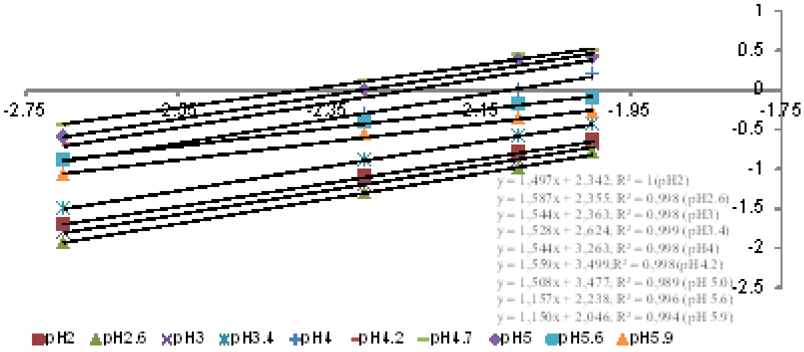

Fig. 5: Variations of logD=f(log(C_{HL}) obtained for different pH values, at C_{NO3}= 10^{-2}M

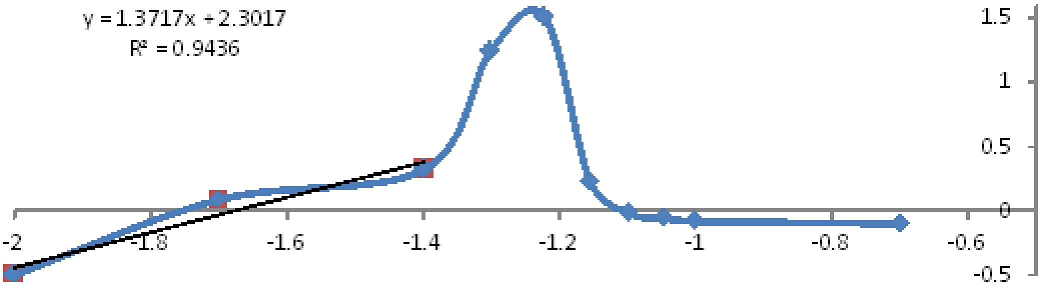

Fig. 6: Variation of logD=f (log (C_{NO3}) obtained at pH=2, for C_{HL}=0.01mol/kg

extraction reaction of the predominant Zn^{2+} specie by 3-methyl-quinoxaline-2-thione symbolizedas $\overline{LH}$ in following, combinesion-pair formation and ionic exchange mechanisms. These reactionsare expressed by the general equations

$$Zn^{2+} + l\,\overline{(LH_2^+NO_3^-)} \longleftrightarrow \overline{Zn(LH_2)_l(NO_3)_l^{2+}} \quad (8), \quad l = 1;2 \quad \text{for pH} < 3$$

$$Zn^{2+} + l\,\overline{LH} + nH_2O \longleftrightarrow \overline{Zn(LH)_l\,H_{-n}^{(2-n)+}} + nH_3O^+ (9), \quad l = 1;2 \quad \text{for } 3 \leq pH \leq 4.7$$

In the above equations, the onlined entities refer to organic phase and$n$= 0; 1; 2; etc. The symbol H_{-n} stands both for hydrogen atoms (n< 0) and for OH group (n> 0).

The corresponding D expression being

$D = \frac{[\overline{Zn}]}{[Zn^{2+}]}$ (10) With $[\overline{Zn}]$= $\left[\overline{Zn(LH_2)_l(NO_3)_l^{2+}}\right]$ or $\left[\overline{Zn(LH)_l\,H_{-n}^{(2-n)+}}\right]$

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

$$K_{0l} = \frac{\left[\overline{Zn(LH_2)_l(NO_3)_l^{2+}}\right]}{[Zn^{2+}]\left[\overline{(LH_2^+NO_3^-)}\right]^l} = \frac{\left[\overline{Zn(LH_2)_l(NO_3)_l^{2+}}\right]}{[Zn^{2+}]\left[\overline{LH_2^+}\right]^l[NO_3^-]^l} \qquad (11)$$

Equation (10) can be rearranged in the form

$$D = K_{0l}\left[\overline{LH_2^+}\right]^l[NO_3^-]^l \qquad (12)$$

Assuming, in first approximation, that $\left[\overline{Zn(LH_2)_l(NO_3)_l^{2+}}\right] = C_{LH}$ and $[NO_3^-] = C_{NO_3}$ we obtain

$$\log D = \log K_{0l} + l \log C_{HL} + l \log C_{NO_3} \qquad (13)$$

For ionic exchange mechanism (9) the extraction constant, $K_{nl}$is

$$K_{nl} = \frac{\left[\overline{Zn(LH)_lH_{-n}^{(2-n)+}}\right][H^+]^n}{[Zn^{2+}][\overline{H_2L}]^l} \qquad ...(14)$$

and D is given by:

$$D = \frac{\left[\overline{Zn(LH)_l\,H_{-n}^{(2-n)+}}\right]}{[Zn^{2+}]} = K_{nl}[\overline{H_2L}]^l[H^+]^{-n} \quad ...(15)$$

Taking into account the approximations given above, logD can be expressed as:

$$\log D = \log K_{nl} + npH + l\log C_{LH} \quad ...(16)$$

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

$$\log A = \log K_{nl} + m\log C_{HNO_3} + npH$$

$$\log D = \log K_{nl} + m\log C_{NO_3} + npH + l\log C_{HL} \quad ...(17)$$

Where$m$ = $l$and n=0 for pH< 3, and m= 0and n"" 0 in the pH range of 3≤ pH ≤ 5.6.

At given C_{NO_3} and pH, equation (17) can be written as:

$$\log D = \log A + l\log C_{HL} \quad ...(18)$$

with ...(19)

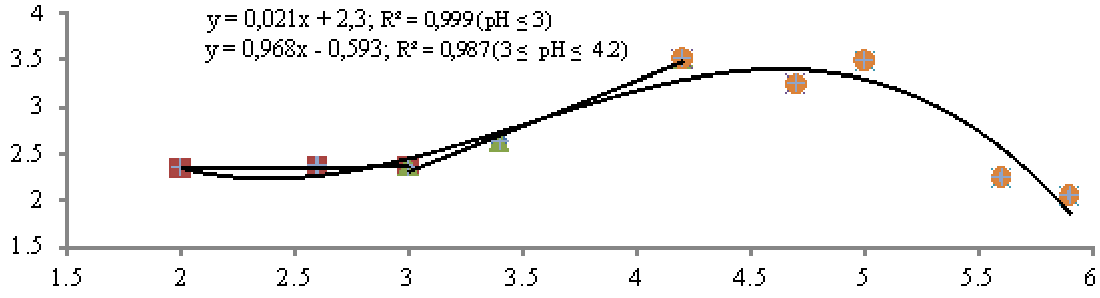

Fig. 7: Variations of logA = f(pH)

Whereas at fixed C_{HL} and pH, the expression of logD becomes

$$\log D = \log B + m\log C_{HNO_3} \quad ...(20)$$

with ... (21)

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:

$$\frac{\delta \log D}{\delta \log C_{LH}} = l \quad ...(22)$$

$$\frac{\delta \log D}{\delta \log C_{NO_3}} = m \quad ...(23)$$

$$\frac{\delta \log D}{\delta pH} = \frac{\delta \log A}{\delta pH} = n \quad ...(24),$$

From results obtained at pH=2,logC_{HL}=-2, and $C_{NO_3} \le 0.07M$ (***Figure 6***.), the straight line

is of a slope . This result is in

consistent with that of logD=f(logC_{HL}) (*Figure 5*.) obtained at pHd” 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_{NO3}=10^{-2}M *(Figure 7).*Straight lines having slopes of 0 and 1 are obtained respectively, at pH < 3 and 3 ≤ pH ≤ 4.7. 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$^+$exchangereaction, in low acidic medium (3 ≤ pH ≤ 5). As discussed above, both ion-pair and ionic exchange reactions rise from a combination of at least two predominant reactions with *l* = 1 and 2.The apparent extraction constants, $K_{n1.5,}$ could be determined by experiment, taking into account that m value. isof 1.4and 0, respectively for pH < 3 and 3 ≤ pH ≤ 5.These constants are evaluated from intercepts of the logA=f(pH) straight lines allowing us to obtainlog$K_{01.5}$ = 5.1, and log$K_{11.5}$ = -0.6. As found,the log D=f($\log C_{NO_3}$) (*Figure 5)* and logA=f(pH) (*Figure 6)* straight lines obtained respectively at $\log C_{NO_3}$ ≤ -1.4 and pH ≤ 3 have the same ordinate at the origins,confirming also that *m=l*and *n*=0, because we have $\log C_{HNO_3}$ = $\log C_{HL}$= -2.

Taking into consideration the molar fraction (x) of extraction mechanism with 1 chelatant molecule, the overall partition equilibrium involving ion-pair formation, issummarized by the following reaction:

$$x\left(\mathrm{Zn}^{2+} + \overline{(\mathrm{LH}_2^+ NO_3^-)} \longleftrightarrow \overline{Zn(LH_2)(\mathrm{NO}_3)^{2+}}\right), \quad (K_{01})^x \quad (25)$$

$$(1 - \mathrm{x})\left(\mathrm{Zn}^{2+} + 2\,\overline{(\mathrm{LH}_2^+ NO_3^-)} \longleftrightarrow \overline{Zn(LH_2)_2(\mathrm{NO}_3)_2^{2+}}\right), (K_{02})^{1-x} \quad (26)$$

$$\mathrm{Zn}^{2+} + \quad (2 - x = m)\,\overline{(\mathrm{LH}_2^+ NO_3^-)} \longleftrightarrow \overline{Zn(LH_2)_l(\mathrm{NO}_3)_l^{2+}}, \quad K_{o0verall}, \quad 1 \le l \le 2 \quad (27)$$

Knowing that the positively charged species could be neutralizedby NO_3^- anion, as observed for other similar organic complexes [31], the reaction (27) becomes: $+ l\log C_{HL} + n\mathrm{pH}$ 1.4 $\int \log C_{NO_3}$

$$\mathrm{Zn}^{2+} + 2(B^+, NO_3^-) + (2 - x = m)\,\overline{(\mathrm{LH}_2^+ NO_3^-)^{2+}} \longleftrightarrow \overline{Zn(LH_2)_m(\mathrm{NO}_3)_{m+2}} + 2B^+ \quad (28)$$

And B^+ is $H^+ or\ Na^+$

While the overall 1H$^+$ exchange reactionis expressed as

$$x\left(\mathrm{Zn}^{2+} + \overline{\mathrm{LH}} \longleftrightarrow \overline{\mathrm{ZnL}^+} + 1\mathrm{H}^+\right) \quad (\mathrm{K}_{11})^{\mathrm{x}} \quad (29)$$

$$(1 - x)\left(\mathrm{Zn}^{2+} + 2\,\overline{\mathrm{LH}} + \mathrm{H}_2\mathrm{O} \longleftrightarrow \overline{\mathrm{Zn(L)(LH)}^+} + 1\mathrm{H}_3\mathrm{O}^+\right) \quad (\mathrm{K}_{12})^{1-\mathrm{x}} \quad (30)$$

$$\mathrm{Zn}^{2+} + \quad (2 - \mathrm{x} = \mathrm{l})\,\overline{\mathrm{LH}} + \mathrm{H}_2\mathrm{O} \longleftrightarrow \overline{\mathrm{Zn(L)(LH)}_{l\text{-}1}^+} + 1\mathrm{H}_3\mathrm{O}^+, \quad \mathrm{K}_{1\mathrm{overall}}, \quad 1 \le l \le 2 \quad (31)$$

log$K_{1overall}$=log$K_{11.5}$= xlogK_{11} + (1-x)logK_{12} (32)

The molar fraction (x) can be obtained experimentally according to *l*= 1.5 = 2 - x forpH d” 4.7, in these conditions. Thus, thexvalues of1:1 Zn-$\overline{\mathrm{LH}}$ and 1:2 Zn- extracted species are of 0.5, in all cases. Accordingly, both ion-pair and ion exchange extractedcomplexes, involve 50% of and $\overline{\mathrm{Zn(LH_2)_2(NO_3)_2^{2+}}}$ and, $\overline{\mathrm{ZnL}^+}$ and, respectively. Similar complexes with 1:1or 1:2divalent metal-schift base ligandstoichiometry 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 stoechiometryand the stability constants of the extracted Zn^{2+} 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 stoechiometry 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 isevaluated. It is foundthat 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 C_{NO_3} , and reaches a maximum of 97% at C_{NO_3} = 0.07M / pH=2.

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