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Liquid-Liquid Extraction of Cadmium by 3-Methyl-Quinoxaline-2-Thione from Phosphoric Medium

Chemistry

KEYWORDS : liquid-liquid extraction, 3-methyl-quinoxaline-2-thione, cadmium, phosphoric acid, extraction mechanism.

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ABSTRACT

Recovery of cadmium with3-methyl-2-quinoxaline-2-thione (LH) from phosphoric acid is investigated as a function of pH, and analytical concentration of Cd(II), and extractant (C_(LH)). A recovery of 70 to 80% is achieved with LH 0.13 and 0.26M at pH 3.5. Extraction is a complex process which often results in combining two predominant reactions that conventional slope analysis cannot directly be used to determine the extracted species. A novel approach towards this technique is examined with combining stoechiometry variation of

$Cd\text{-}H_3PO_4$, Cd-LH complexes, H^+ and/or OH^- exchange, with pH. The extracted species are found to be $\overline{Cd(H_2PO_4)_N(LH_2)_lX_{l-N}{}^{(2-N)+}}$, NX^-, where l= 3; 4; N=0 ; 1 and $X^- = NO_3^-$ or $H_2PO_4^-$, for pH≤3, $\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_3}$, $\overline{Cd(OH)(H_2PO_4)(LH)_3}$ = $\overline{Cd(H_2PO_4)L(LH)_2}$, $\overline{Cd(H_2PO_4)(H_3PO_4)L(LH)_2}$, $\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_3}$, $\overline{Cd(H_2PO_4)_2(L)_2}$, $\overline{Cd(H_2PO_4)_2(LH)_2}$ = $\overline{Cd(H_2PO_4)(H_3PO_4)L(LH)}$, $\overline{Cd(H_2PO_4)_2(LH)_2H_1}$ = $\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_2}$, $\overline{Cd(H_2PO_4)_2L(LH)}$ = $\overline{Cd(H_2PO_4)(H_3PO_4)L_2}$, $\overline{Cd(H_2PO_4)(H_3PO_4)LH}$, $\overline{Cd(OH)(H_2PO_4)LH}$, for 3 < pH < 7. The formation constants of these species are determined.

Introduction

Heavy metals are naturally occurring elements that are of a major concern in environmental chemistry. Among these elements, cadmium is considered as one of the most toxic trace elements in the environment and is ranking among groups of chemicals of major public health concern. The World Health Organization has recommended a cadmium consumption limit of 57 µg and 70 µg per day per capita [1]. The presence of Cd(II) in soils is a result , in particular, of fertilizers uses in agricultural production. This element is then severely controlled in environment that its input on agricultural lands through fertilizers is limited in several countries [2]. Most environmental regulations state that cadmium should not exceed 20 ppm in the fertilizer [3]. The natural cadmium concentration in phosphates ranges from 3 to 100 µg/g [4]. The production of phosphoric acid, which is an intermediate compound in the production of fertilizers, is based on the leaching procedure [1,2], commonly designated a "wet process". During the sulfuric acidulation of phosphate rock [5], cadmium is dissolved in leaching solution. This results in a manufacture of contaminated fertilizer which final Cd(II) concentration is not different from that in raw material (phosphate rock)) [6-8]. This toxic element is therefore detrimental to fertilizer industry, that reducing its content is crucial procedure, in this case. This can be achieved either by using raw materials with a lower cadmium content, or by eliminating the cadmium from the phosphate rock or the phosphoric acid during the production process. Using low-Cd rock has been the major strategy in fertilizers industry where cadmium reduction policies are being pursued. Nevertheless, decadmiation is currently too expensive and low-cost technologies are not yet fully developed [9]. Wet process phosphoric acid has to be purified that Cd(II) removal from this medium is then essential and given much considerations. Numerous processes have been used for this purpose using chemical precipitation, adsorption, ion exchange, and solvent extraction. Among these methods liquid-liquid extraction is the most promising process for the separation and recovery of metals from the complex media, for being one of the most economical and practical processes. Extraction of cadmium from H3PO4 is undertaken using high molecular weight amines and/or phosphoric, (RO)2P02H,phosphonic, (RO)(R)P02H, and phosphinic, (R)2P02H, acid extractants [6-7]. In general, the removal process carried out in these conditions involves aqueous cadmium chloro-complexes and is consequently, a function of halogen ion concentration. As discussed previously, extracting reagents combining different extraction phenomena are more suitable to achieve a best heavy metal recovery in a large pH interval [10-11].Recently it is found that removal of some divalent heavy metals such as Zn2+, with quinoxaline-2-thione involves complexing phenomenon, ion-pair formation, and H+ exchange reaction. Obtained partition coefficient is much less sensitive to both acidity at pH < 3.0, and nitrate concentration (CNO3) for CNO3 higher than 0.1M [12].

Taking into account these considerations, the extraction of Cd(II) from phosphoric acid media using 3-methyl-2 (1H)-quinoxalinethione (LH) is studied in pH range of 2 to 6, and analytical concentrations of H_3PO_4, and LH reagent ranging, from 0.026 to 0.26M, and 2.5 to 7.2M, respectively.

2. EXPERIMENTAL

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

A stock solution of 10-3mol/l Cd (II) is obtained by dissolution of known amount of Highly pure Cadmium Nitrate Hexahydrate in adequate volume of diluted laboratory phosphoric acid A solution of synthesized extractant is prepared with dissolution of 0.26mol/l 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 [12-15].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-méthylquinoxalin-2 (1H), which is purified by re-crystallization. Reaction of obtained compound with P_2S_5 in refluxing pyridine for four hours gives 3-methyl-2 (1H)-quinoxalinethione (Rdt : 75%). (Figure 1)

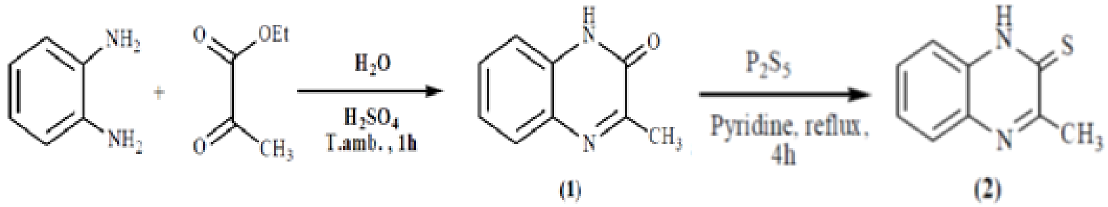

Fig. 1. Reaction of condensation of o-phenylenediamine and 1,2-diketones and sulfidation of the 3-methyl quinoxalin-2-thione ($\overline{LH}$) [12-15].

2.2. 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 15min. 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 KOH/HNO3, and measured before and after extraction test. After equilibration, the separator funnel is left standing for at least 30 min for completing phase separation.

The extraction experiments are carried out at room temperature, as a function of pH, and concentrations of phosphoric acid, and extractant, designated thereafter as $C_{H_3PO_4}$ and $C_{\overline{LH}}$, respectively.

The aqueous cadmium is analyzed using Benchtop XRF Spectrometer with X-LabPro Version 4.0 software. The concentration of cadmium in the organic phase was calculated from material balance.

The distribution ratio is calculated from the relationship:

$$D = \frac{\overline{\left[\mathrm{Cd}^{2+}\right]}}{\left[\mathrm{Cd}^{2+}\right]} \quad (1)$$

Where $\left[\overline{\mathrm{Cd}^{2+}}\right]$ and $[\mathrm{cd}^{2+}]$ denote the concentration (mol /)of cadmium in the organic and aqueous phases, respectively

3. RESULTS AND DISCUSSION

3.1. Effect of equilibrium pH

Fig. 1 reproduces the logarithmic variation of D with pH for H_3PO_4 3.22M, in the pH range of 1.5 to 7, and initial chelatant concentration ($C_{\overline{LH}}$) of 0.05, 0.13, and 0.26M. As shown logD increases with pH, to reach a maximum at pH_{max}, and then decreases as pH continues to rise, for $C_{\overline{LH}} = 0.13$ and 0.26 M. A steady logD value of about zero is observed for pH ≥3, for $C_{\overline{LH}} = 0.05$ M. Maximum recovery efficiencies are found to rise with $C_{\overline{LH}}$ whereas optimum pH_{max} of 3.5 is obtained in all the cases. Optimal Cd(II) recovery of about 72 to 80% is obtained with $C_{\overline{LH}} = 0.13$ and 0.26 M. Distinct pH segments with continuous varying slopes suggest that cadmium extraction rises from different reactions.

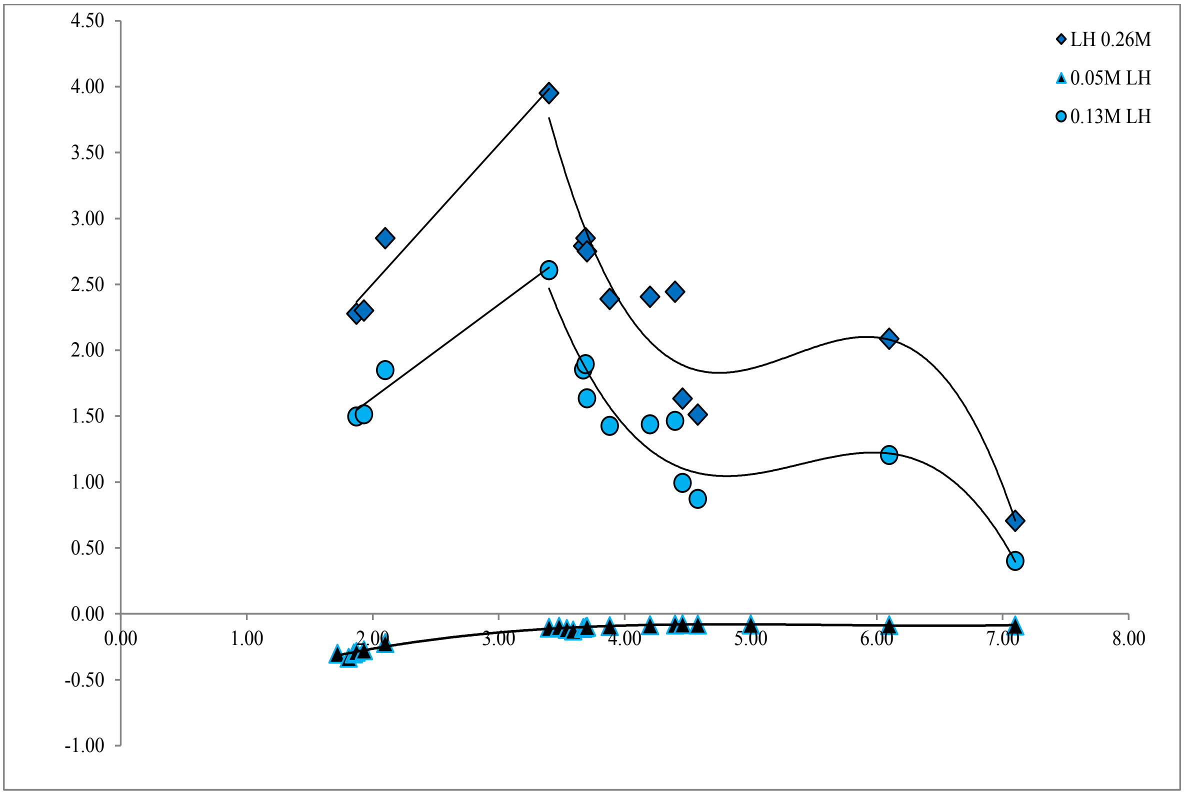

Fig.1.Variation of logD versus pH, at$C_{\overline{LH}} = 0.05,\ 0.13,$ and0.26M, in 3.22M H_3PO_4.

Effect of initial cadmium concentration on the removal efficiency is investigated in 3.22M H_3PO_4, with LH concentration of 0.3M. The results are shown in Fig. 2.

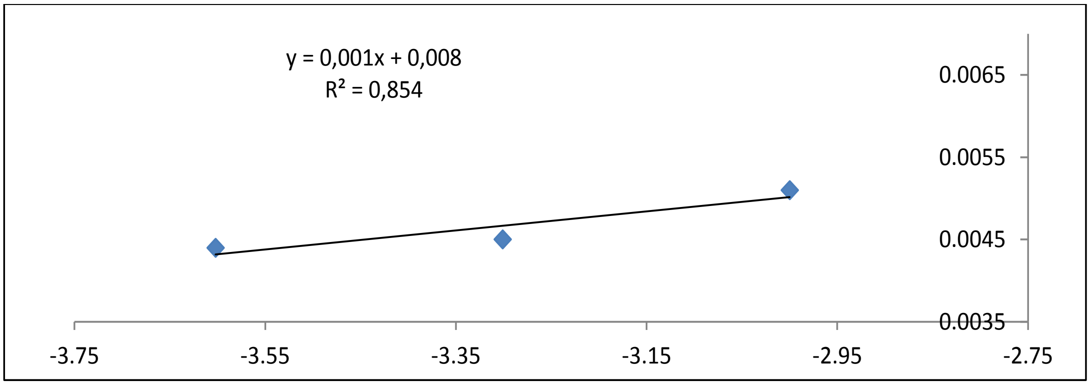

Fig.2. Variation of logD=f(logC_{Cd}), obtained at $C_{\overline{LH}} = 0.3$M, in 3.22M H_3PO_4.

As observed, with increasing initial cadmium concentration of 2.5x10^{-4}–10^{-3} M, steady removal efficiency is obtained, indicating no formation of less-extractable polymeric

3.2. Effect of extractant concentration

Fig. 3 reproduces the logarithmic variation ofD with $C_{\overline{LH}}$,at different pH values, for H_3PO_4 3.22M. These variations are linear with slopes varying in the range of about 1 to 3.7.

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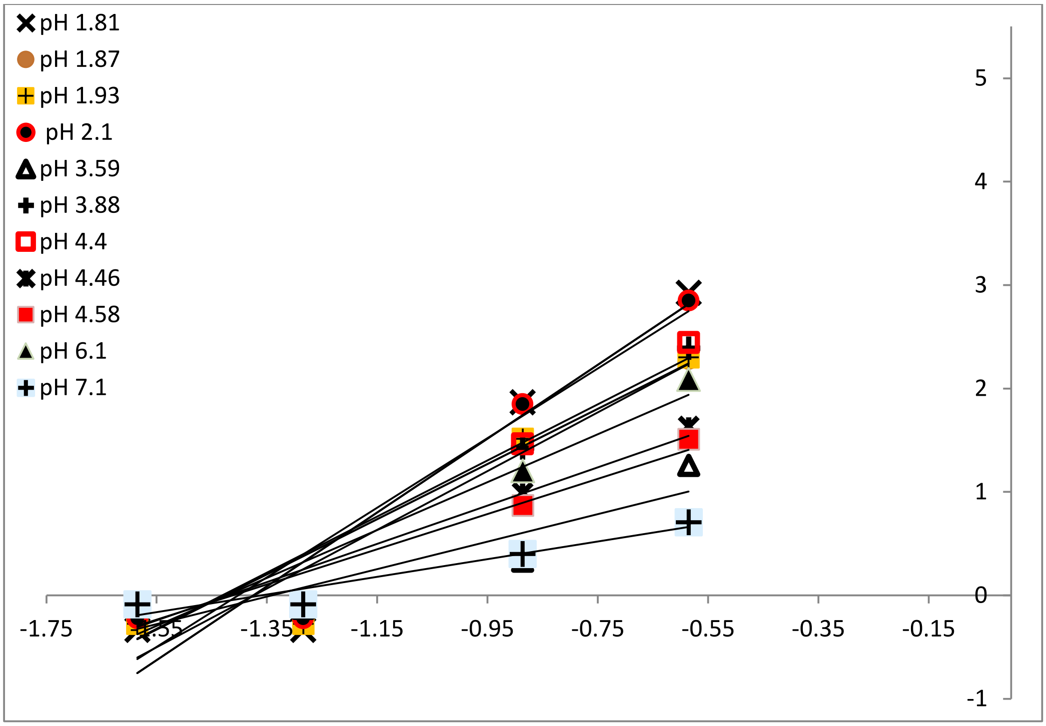

Fig. 3.Variation of log D with the LH analytical concentration $C_{\overline{LH}}$, at $C_{H_3PO_4}$= 3.22M

From these results, the extraction reaction stoichiometry is not integer as could be expected from theoretical single reaction. Similar results are observed previously for zinc and some rare earths extraction with 3-methyl-quinoxaline-2-thione [12], and carboxylic acids, respectively [18].

As discussed above, it can be assumed that cadmium extraction rises from different reactions, and consequently results in a combination of at least two predominant extracted complexes.

Apparent equilibrium constants, $K_{ap} = K_{l,\,n}$ can be obtained from the origin ordinates which are $A = \log K_{l\,n} + n\,pH$.

3.3. Cadmium extraction from phosphoric acid solutions

As previously discussed, the extraction reaction of divalent metals, such as Zn^{2+}, with 3-methyl-quinoxaline-2-thione (LH) combines ion - pair formation and ionic exchange mechanisms. A general expression of these extractions is:

$$Cd^{2+} + l\,\overline{(LH_2^+X^-)} \rightleftarrows \overline{Cd(LH_2)_l(X)_l^{2+}} \;:\; K_{l,0}\ (2)$$

$$Cd^{2+} + l\,\overline{(LH_2^+X^-)} + nH_2O \rightleftarrows \overline{Cd(LH_2)_lX_lH_{-n}^{(2-n)+}} + n\,H_3O^+ \;:\; K_{l,n}\ (3)$$

where X^- is aqueous anionic ligand (NO_3^- and $H_2PO_4^-$) , the onlined entities refer to organic phase, and n = 0;1;2,etc…The symbol H_{-n} stands both for hydrogen (n<0) and for OH group (n>0). The D expression is given by:

$$\mathrm{D} = \frac{[\overline{\mathrm{Cd}}]}{[\mathrm{Cd}^{2+}]}\ (4)$$

$$[\overline{\mathrm{Cd}}] = \overline{\mathrm{Cd(LH_2)}_l\mathrm{(X)}_l^{2+}} + \overline{\mathrm{Cd(LH_2)}_l\mathrm{X}_l\mathrm{H}_{-\mathrm{n}}}^{(2-\mathrm{n})+}\ (5)$$

The extraction constants for equilibriums (2) and (3) are respectively:

$$\mathrm{K}_{l0} = \frac{[\overline{\mathrm{Cd(LH_2)}_l\mathrm{(X)}_l^{2+}}]}{[\mathrm{Cd}^{2+}][(\mathrm{LH_2^+X^-})]^l}\quad (6)$$

$$\mathrm{K}_{l\mathrm{n}} = \frac{[\overline{\mathrm{Cd(LH_2)}_l\mathrm{H}_{-\mathrm{n}}^{(2-\mathrm{n})+}}][\ \mathrm{H}^+]^\mathrm{n}}{[\mathrm{Cd}^{2+}][(\mathrm{LH_2^+X^-})]^l}\quad (7)$$

Assuming in first approximation that $[\overline{(\mathrm{LH_2^+X^-})}] = \mathrm{C}_{\overline{\mathrm{LH}}}$ we obtain a general expression:

$$\log\mathrm{D} = \log\mathrm{K}_{l,\mathrm{n}} + l\log\mathrm{C}_{\overline{\mathrm{LH}}} + \mathrm{n\ pH}\qquad (8)$$

where n = 0, for ion-pair formation.

The variation of the distribution coefficient according to pH allows us to define the nature of $\mathrm{C}_{l;\mathrm{n}}$ extracted species according to expressions:

$$\left(\frac{\delta\log\mathrm{D}}{\delta\mathrm{pH}}\right)_{\mathrm{C}_{\overline{\mathrm{LH}}}} = \mathrm{n}$$

$$\left(\frac{\delta\log\mathrm{D}}{\delta\log\mathrm{C}_{\overline{\mathrm{LH}}}}\right)_{\mathrm{pH}} = l$$

So, the extracted complexes, noted thereafter (*l*; n), can be well described from experimental data logD = f(pH), Fig.1. For this purpose, fitting data to a polynomial equation is carried out at $\mathrm{C}_{\overline{\mathrm{LH}}} = 0.13$ and 0.26M, for pH region of 3.5-7.0, where in more acidic conditions, results fit a straight line with slope of 0.7 to 1.0. At $\mathrm{C}_{\overline{\mathrm{LH}}} = 0.05$M results are fitted to a second degree equation, in all explored conditions. Fig. 5 shows plots of $\left(\frac{\delta\log\mathrm{D}}{\delta\mathrm{pH}}\right)_{\mathrm{C}_{\overline{\mathrm{LH}}}} = \mathrm{n=f(pH)}$, obtained in these conditions.

In addition, the molar ratio metal: LH is varying continuously in extracted entities with aqueous solution acidity, as seen above. To define the nature of these species requires to carry out *l*= f(pH) (Fig. 5), which is given by the variation of the straight line slopes of logD=log $\mathrm{C}_{\overline{\mathrm{LH}}}$, (Fig.1) with pH.

From these results, cadmium recovery reaction is influenced by extractant concentration and aqueous media acidity as found previously for extraction of yttrium by phenylacetic acid in toluene [17]. So this recovery is achieved only with solvatation phenomena, at $\mathrm{C}_{\overline{\mathrm{LH}}} = 0.05$M.. Whereas during Cd(II) remove with LH 0.13, and 0.26M, ion exchange is involved showing, a maximal H^+ exchange at pH lower than 2, while OH^- exchange increases with pH to reach maximal values of about 2 or 2.5, at pH~ 4 , and then decreases when the pH continues to rise. In addition, cadmium extraction is carried out in low acidic to neutral condition with no ionic exchange process for pH ranging from 5 to 6, and with exchange of 2 or 3 OH^- at pH 7.Taking into account l=f(pH) variation, the predominant (l, n) extracted species are (4, 1), (3, 1), (3, -2), (3, -3), (2, 0), (1, 0) , (1, -2) et (1, -3).

3.4. Evaluation of $K_{l,\,n}$

As discussed above apparent equilibrium constants can be obtained from the origin ordinates of logD=f(log$C_{\overline{LH}}$) which are A = log$K_{l n}$ + n pH.

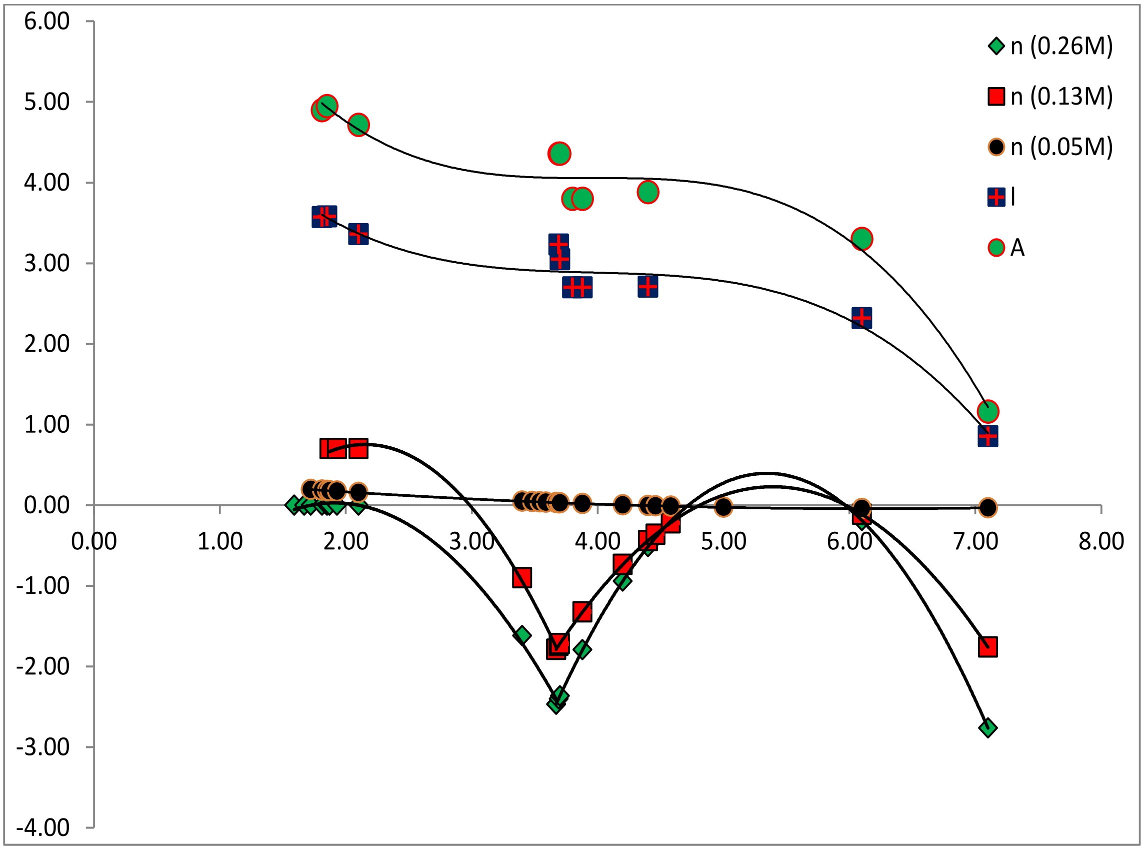

Fig.5. Variations of l, n, and A versus pH, obtained for H_3PO_4 3.22M, at $C_{\overline{LH}} = 0.05, 0.13,$ and 0.26M.

As can be seen, plots of A=f(pH) (Fig.5) fit a third degree polynomial. As a result, the equilibrium extraction constants $K_{l,\,n}$ cannot be obtained directly from ordinates at the origin of the curve A = f(pH). The computation of $K_{l\,,\,n}$ (=A – n pH) constants is performed on the basis of these curves for different (l , n) overall reactions. Table I shows obtained results. It is interesting to indicate that $|n|$ represents also the predominant H^+ or OH^- exchange reactions, contributing to overall equilibrium. For two successive (l, i) and (l, j), or (l_1, n) and (l_2, n) complexes, the apparent constants of this equilibrium are given by the relations

$$K_{ap} = (K_{l,i})^{(1-x)}(K_{l,j})^{x} \quad \text{or} \quad K_{ap} = (K_{l_1,\ n})^{(1-x)}(K_{l_2,\ n})^{x} \qquad (9)$$

$$\text{With } x = |n-i| \text{and } |j| = |i| + 1 \text{ or } x = l - l_1 \ \ and\ l_2 = l_1 + 1 \qquad (10)$$

As example, taking into consideration the molar fraction (x) of extraction mechanism with 2 chelatant molecules, the overall partition equilibrium involving successive exchange reactions n= 0 and -1 , is summarized by the following reaction:

$$(1-x)\ (Cd^{2+} + 2\overline{(LH_2^+X^-)} \rightleftarrows \overline{Cd(LH_2)_2(X)_2^{2+}}\ : (K_{2,0})^{(1-x)};\ i = 0 \qquad (11)$$

$$x\left(Cd^{2+} + 2\ \overline{(LH_2^+X^-)} + H_2O \rightleftarrows \overline{Cd(LH_2)_2X_2H_1^{3+}} + 1\ OH^-\right): (K_{2,-1})^{(x)};\ j = -1 \qquad (13)$$

$$Cd^{2+} + 2\ \overline{(LH_2^+X^-)} + nH_2O \rightleftarrows \overline{Cd(LH_2)_2H_{-n}^{(2-n)+}} + n\ OH^-\ ) :\ K_{app}\ ;\ -1 \leq n \leq 0 \quad (14)$$

$$\log K_{app} = (x)\log K_{2,-1} + (1-x)\log K_{2,0}, \text{with } x = |n-1|$$

This allows us to calculate the equilibrium constants for no predominant species combined in overall mechanism for which the value of $\log K_{l,\,n}$ can be known. So, logarithmic values of $K_{2,-1}$, $K_{2,0}$, and $K_{4,0}$ are determined by using the values of $\log K_{l,\,n}$ obtained from (Fig.5) :

$$\log K_{2,-0.5} = 0.5\log K_{2,-1} + 0.5\log K_{2,0} = 6.05 \Rightarrow \log K_{2,-1} = 8.9$$

$$\log K_{1.5,-1} = 0.5\log K_{2,-1} + 0.5\log K_{1,-1} = 8.9 \Rightarrow \log K_{1,-1} = 8.9$$

$$\log K_{3.4,\ 0} = 0.6\log K_{4,0} + 0.7\log K_{3,0} = 4.71 \Rightarrow \log K_{4,0} = 5.78$$

$$\log K_{3,-2.3} = 0.3\log K_{3,-2} + 0.7\log K_{3,-3} = 12.81 \Rightarrow \log K_{3,-3} = 13.54$$

Taking into account the protonation of amino group at pH <3 [12], and percentage distribution of phosphoric complexes of cadmium versus pH [16], predominant extraction reactions are summarized in Table I.

(*l*, n)	Extraction reaction	log K*l*, n
(4,0)	**pH ≤ 3** $Cd(H_2PO_4)_N^{(2-N)+} + 4\ \overline{(LH_2^+\ X^-)} \rightleftarrows \overline{Cd(H_2PO_4)_N(LH_2)_4X_{4-N}{}^{(2-N)+}} + NX^-$; N= 0; 1	5.78
(3,0)	$Cd(H_2PO_4)_N^{(2-N)+} + 3\ \overline{(LH_2^+\ X^-)} \rightleftarrows \overline{Cd(H_2PO_4)_N(LH_2)_4X_{3-N}{}^{(2-N)+}} + NX^-$; N= 0; 1	4.15
(3,-1)	**3 < pH <** 7 $Cd(H_2PO_4)_2 + 3\ \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(H_2PO_4)_2(LH)_3H_1} + OH^-$ $Cd(OH)_2(H_2PO_4)_2^{2-} + 3\ \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(OH)_2(H_2PO_4)(LH)_3H_1} + H_2PO_4^- + OH^-$	7.15
(3,-2)	$Cd(OH)_2(H_2PO_4)_2^{2-} + 3\ \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(OH)_2(H_2PO_4)_2(LH)_3H_2} + 2OH^-$	11.1
(3,-3)	$Cd(OH)_2(H_2PO_4)_2^{2-} + 3\ \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(OH)_2(H_2PO_4)_2(LH)_3H_3} + 3OH^-$	13.54*
(2,0)	$Cd(H_2PO_4)_2 + 2\ \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(H_2PO_4)_2(LH)_2H_0}$	3.0*

(2,-1)	$Cd(H_2PO_4)_2 + 2\,\overline{LH} + H_2O \rightleftarrows \overline{Cd(H_2PO_4)_2(LH)_2H_1} + OH^-$ $Cd(OH)_2(H_2PO_4)_2^{2-} + 2\,\overline{(LH)} + H_2O \rightleftarrows \overline{Cd(OH)_2(H_2PO_4)_2(LH)_2H_1} + OH^-$	8.9*
(1,-1)	$Cd(H_2PO_4)_2 + \overline{(LH)} + H_2O \rightleftarrows \overline{Cd(H_2PO_4)_2(LH)H_1} + OH^-$ $Cd(OH)_2(H_2PO_4)_2^{2-} + \overline{(LH)} + H_2O$ $\rightleftarrows \overline{Cd(OH)_2(H_2PO_4)(LH)H_1} + H_2PO_4^- + OH^-$	3.0

Table I. Equilibrium constants of cadmium extraction by 3-Methyl Quinoxaline-2-thione from H_3PO_4 3.22M. X=NO_3^- and/ or $H_2PO_4^-$, and N= 0; 1 and 2. .* Calculated constant

One can note that positively charged species are neutralized by NO_3^- or $H_2PO_4^-$ anions, as observed for other similar organic complexes [12]. Moreover, it is known that $H_2PO_4^-$ specie can act as bidental ligand, and Cd(II) has a coordination number equal to 6, 5, and 4. Accordingly we propose to formulate the identified extracted complexes ($C_{l\,n}$) as shown in Table I.

Species C_l n	Extracted complexes
C_{40}	$\overline{\overline{Cd(LH_2)_4X_4}}^{2+}, 2X^-; \overline{Cd(H_2PO_4)(LH_2)_4X_3}^{+}, X^-; (X \equiv NO_3^-$ and/or $H_2PO_4^-)$
C_{30}	$\overline{\overline{Cd(LH_2)_3X_3}}^{2+}, 2X^-; \overline{Cd(H_2PO_4)(LH_2)_3X_3}^{+}, X^-; (X \equiv NO_3^-$ and/or $H_2PO_4^-)$
$C_{3\text{-}1}$	$\overline{\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_3}}, \overline{Cd(OH)(H_2PO_4)(LH)_3} \equiv \overline{Cd(H_2PO_4)L(LH)_2}$
$C_{3\text{-}2}$	$\overline{Cd(H_2PO_4)(H_3PO_4)L(LH)_2}$
$C_{3\text{-}3}$	$\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_3}$
$C_{2\text{-}0}$	$\overline{Cd(OH)_2(H_2PO_4)_2(LH)_2} \equiv \overline{Cd(H_2PO_4)_2(L)_2}, \overline{Cd(H_2PO_4)(H_3PO_4)L(LH)}$
$C_{2\text{-}1}$	$\overline{Cd(H_2PO_4)(H_3PO_4)(LH)_2}, \overline{Cd(H_2PO_4)_2L(LH)} \equiv \overline{Cd(H_2PO_4)(H_3PO_4)L_2}$
$C_{1\text{-}1}$	$\overline{Cd(H_2PO_4)(H_3PO_4)LH}, \overline{Cd(OH)(H_2PO_4)LH}$

Table II. Extracted complexe formulas

Conclusion

Cadmium removal by 3-methyl-2 (1H)- Methyl Quinoxaline-2-thione (LH) from phosphoric acid (3.22 M), is investigated. The extraction efficiency is dependent on both pH and concentration of chelating reagent. Thus, for 0.13 and 0.26 M LH, extraction efficiency increases with increasing of pH, to reach a maximum at pH around 3.2, and then decreases when pH continues to rise. A recovery of 70 to 80% is found for pH ≤ 3.2, in this case. Whereas a steady recovery of about 50% is observed, for $C_{\overline{LH}} = 0.05$ M , in all explored pH conditions. Extraction reaction is complex process involving Cd-H_3PO_4, Cd-LH complexes, H^+ and OH^- exchange. The stoechiometry and the stability constants of the extracted Cd(II) species is postulated based on a new approach of slope analysis method. Obtained results show that the extraction reaction involves ion pair formation and $1H^+$, 2 and 3 OH^- exchange mechanism. The metal-ligand molar ratios of the prevailing extracted complexes raise from 1:4 to 1:1 as pH increases from 2 to 7.

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