



The Solvent Extraction of Cadmium from Phosphoric Acid Solution By 3-methyl-quinoxaline-2-thione in Toluene as Diluent

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<http://dx.doi.org/10.13005/ojc/320624>

(Received: October 22, 2016; Accepted: November 25, 2016)

ABSTRACT

The solvent extraction of cadmium (II) from phosphoric acid 2.5M by 3-methyl-2 (1H)-quinoxaline-thione ($LH \equiv C_9H_8N_2S$) is investigated in various experimental conditions. Obtained results show a variation of extraction of Cd with pH, and LH concentration. The conventional methods of slope analysis can't be performed successfully for understanding interaction mechanisms. A technique combining slope analysis with the variation of overall extraction constant with pH is performed in this case. There is no predominant removal mechanism, cadmium is extracted as complexes in Cd: LH : H_3O^+ (OH^-) stoichiometry varying between 1:1:0 and 1:3:3. The extraction reaction is a complex process including ion exchange-ion pair formation, organic and inorganic complexation, H_3PO_4 deprotonation and solvation phenomena. A best recovery of 43 to 60% is achieved in acidic conditions with $C_{LH} = 0.26M$.

Keywords: Cadmium, Extraction, Phosphoric medium, pH, 3-methyl-2 (1H)-quinoxaline-thione.

INTRODUCTION

Due to their harmful effects, heavy metals are a major threat to ecological environment, food safety and agriculture sustainable development. As a result, these elements are not suitable in nature that various measures are undertaken to control, and prevent their presence in environment. Among these heavy metals, cadmium is listed as the seventh most toxic substances¹⁻².

Enrichment of Cd in soils is reported, through the land application of bio solids, industrial effluents, and Cd-rich phosphate fertilizers³. In general, phosphate fertilizers are produced by the acidulation of crushed and powdered phosphate.

Thus the removal of Cd(II) from phosphoric acid which is the intermediary product for the production of all high grade phosphate fertilizers, is of ever-increasing interest. Several methods including

precipitation, solvent extraction and ion exchange are proposed in this case.

Amine compounds are successfully used for cadmium separation from complex aqueous media. However, in this extraction system, metal extraction is carried out from acidic media, so that the amine in the organic phase is first converted to its salt. To avoid this limitation on the aqueous condition, quaternary ammonium salts, is employed in neutral, and slightly alkaline. As known the sulfhydryl-containing compounds have the ability to chelate heavy metals such cadmium that Chelating exchangers with thiol functional groups are used for Cd(II) removal from aqueous solutions⁴⁻⁵.

Recently the use of extractants with a bifunctional groups such as quinoxaline-thione for zinc and cadmium removal are highlighted as potential extractant for metal removal from complex aqueous media⁶⁻⁷.

The advantage of this process is that can combine organic and inorganic complexing phenomena, ion-pair formation and ion exchange reactions. Thus, cadmium removal from H_3PO_4 3.22 M is successfully achieved over wide range of pH, in this case. Understanding interaction mechanisms involved in this case, is essential and allows efficient use of solvent extraction procedure⁸.

This interaction is also an actual problem of modern analytical chemistry, which is primordial for environmental sciences, as well as geology, clinical and medicinal chemistry, as discussed previously⁹.

Unfortunately, it is reported that Cd(II) extraction by amines is a variable phenomenon when inorganic complexation is involved in aqueous phase that slope analysis cannot be used to carry out extraction stoichiometry¹⁰. Similar results are obtained for this metal in phosphoric medium⁷. To determine extracted species, a technique combining slope analysis with the variation of apparent extraction constant with pH is performed, in this case. As shown, cadmium removal is essentially achieved via anion-exchange. Obviously to control extraction process in question, more informations are required for the removal of Cd with analytical concentration variation of H_3PO_4 .

For these reasons the present study aims to carry out cadmium extraction reaction predominating in H_3PO_4 2.5M.

MATERIAL AND METHODS

Reagents

All reagents used: $Cd(NO_3)_2$, HCl, NaOH, and H_3PO_4 are of analytical grade and used without further purification. Stock solutions (10^{-3} mol/l) of Cd(II) are prepared by dissolving known amount of cadmium nitrate in adequate volume of 0.1M laboratory phosphoric acid. Initial pH of the aqueous phases, is adjusted using 0.1M KOH or 0.1M HNO_3 , and measured before and after extraction test.

Procedure

The organic and aqueous solutions (H_3PO_4 2.5M) 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. After equilibration, the separator funnel is left standing for at least 30 min for completing phase separation. After equilibration, the separator funnel is left standing for at least 30 min for completing phase separation. The synthesis of 3-methyl-2 (1H)-quinoxaline-thione ($C_9H_8N_2S$) designated thereafter as LH , is performed as described previously⁶⁻⁷. A solution of synthesized extractant is prepared with dissolution of 0.26 mol/l of LH in toluene (C_7H_8).

The extraction of cadmium is studied from aqueous phosphoric acid solutions (2.5M) containing 10-4M Cd(II). All the extraction experiments were carried out at room temperature.

The Cd(II) concentrations in the aqueous phase ($[Cd^{2+}]$) were determined using Benchtop XRF Spectrometer with X-LabPro Version 4.0 software. while the concentration of cadmium in the organic phase ($[Cd]$) was calculated from material balance.

The distribution ratio, D, is calculated as follows:

$$D = \frac{[Cd]}{[Cd^{2+}]} \quad \dots(1)$$

RESULTS AND DISCUSSION

Effect of equilibrium pH

Fig. 1 reproduces the logarithmic variation of D with pH for H_3PO_4 2.5M, in the pH range of about 1.7 to 7.0, and analytical ligand concentration (C_{LH}) of 0.05, 0.13, 0.26, and 0.62M. As can be seen, extraction of cadmium increases with increase in pH to reach a maximum value at pH = 2.1, and after a steady stage observed in the pH range 2.1 – 3.4, logD increases as pH continue to rise. Maxima

are found at pH 3.7 and 4.5, in this case. Extraction yield higher than 66% is achieved at $C_{LH} = 0.62M$, for pH ranging from 2.0 to 5.0. As discussed previously, distinct pH segments with continuous varying slopes suggest that cadmium extraction rises from different reactions⁷.

Effect of extractant concentration

Fig.2 reproduces the logarithmic variation of D with C_{LH} at different pH values, for H_3PO_4 2.5M.

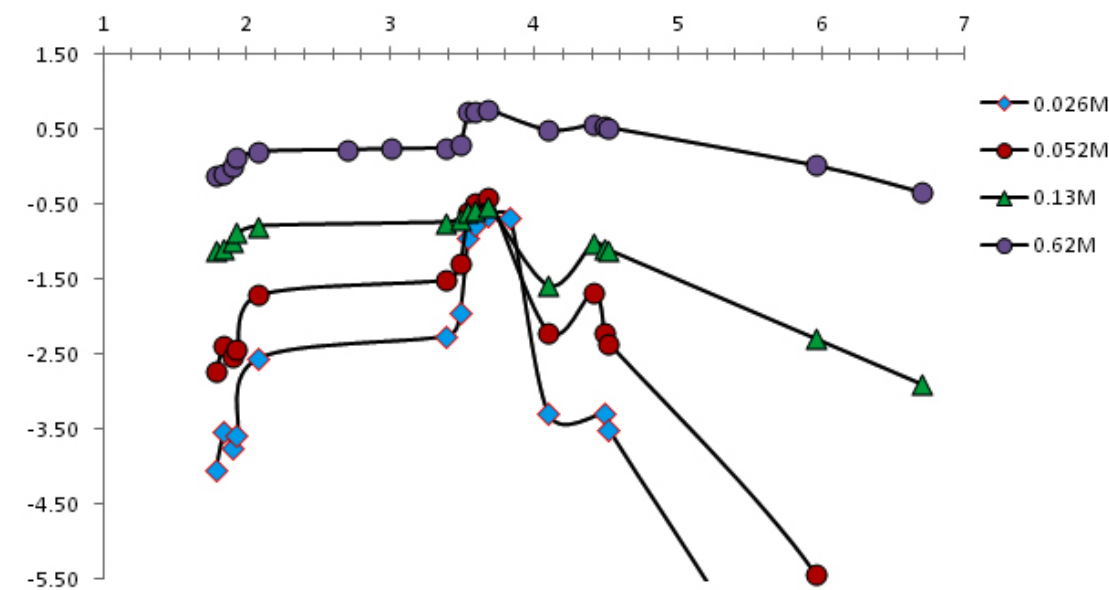


Fig. 1: Variation of logD versus pH, at C_{LH} of 0.05, 0.026M, 0.13, and 0.62M, in 2.5M H_3PO_4

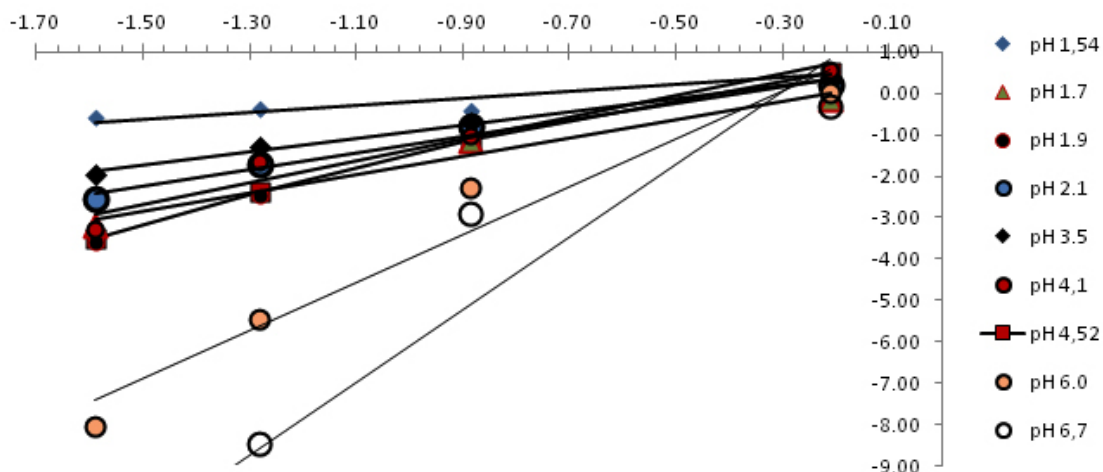


Fig. 2: Variation of log D with the LH analytical concentration C_{LH} , at $H_3PO_4 = 2.5M$, for pH value ranging from 1.5 to 6.7

As found, these variations are linear with slopes varying in the range of about 1 to 6. The overall stoichiometry extraction reaction is not an integer as could be expected from theoretical single reaction. This indicates a variation of extraction of Cd with pH, and LH concentration. Similar

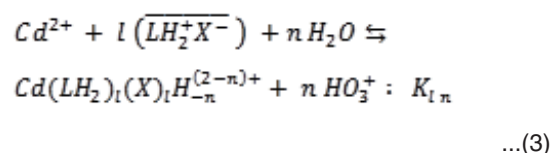
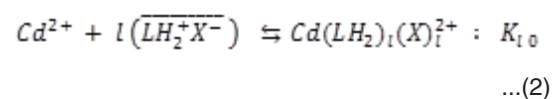
results are observed previously for the extraction of cadmium, zinc and some rare earths by various chelant^{6-7; 10-14}. This shows that at least, two predominant extracted complexes are involved in the removal of Cd (II), in this case.

Cadmium extraction from phosphoric acid solutions

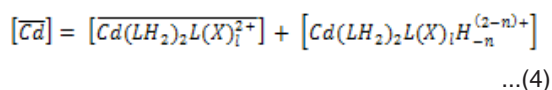
From results obtained previously for Cd(II) removal by 3-methyl-quinoxaline-2-thione⁶⁻⁷, the extraction equilibrium from phosphoric media may be written in the general forms:

Table 1: Equilibrium logarithmic constants ($\log K_{in}$) of cadmium extraction by 3-Methyl Quinoxaline-2-thione from H_3PO_4 2.5M. (* Calculated constant)

(l ; n)	$\log K_{in}$	(l ; n)	$\log K_{in}$
(2.71; 1.01)	-1.06	(1 ; 1)	2.71*
(2.68; 1)	-0.89	(1 ; 2)	-6.73*
(2.68; 1.83)	-2.58	(1 ; 3)	-8.79*
(2.68; 2.88)	-4.60	(2.74;-0.57)	1.50
(2; 0.04)	0.66	(2.74;-1.71)	8.92
(1.6; 0.04)	0.54	(2.74;-2.86)	14.08
(1.6; 0.56)	-1.27	(3 ; -0.57)	3.82
(1.6; 2.36)	-7.54	(3 ; -1.7)	8.93
(2 ; 1)	0.76*	(3;-2.8)	13.90
(2 ; 2)	-5.63*	(3, 0)	1.23*
(2 ; 3)	-13.66*	(3, 1)	-1.72*
(2, -1)	4.53 *	(3, 2)	-0.73*
(2, -2)	8.12*	(3, 3)	-1.67*
(2, -3)	10.53*	(3,-1)	5.8*
(1.0; 0.0)	0.77	(3,-2)	10.3*
(1.0; 2.2)	-7.12	(3,-3)	14.8*
(1; 0.75)	-2	(1 ;2)	-6.73*
(1; 1.5)	-4.76	(1 ;3)	-8.79*



Where X^- is aqueous anionic ligand, 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 ($n > 0$). K_{ln} denotes the constant of equilibrium reaction. The extracted species are given by:



K_{ln} is given by :

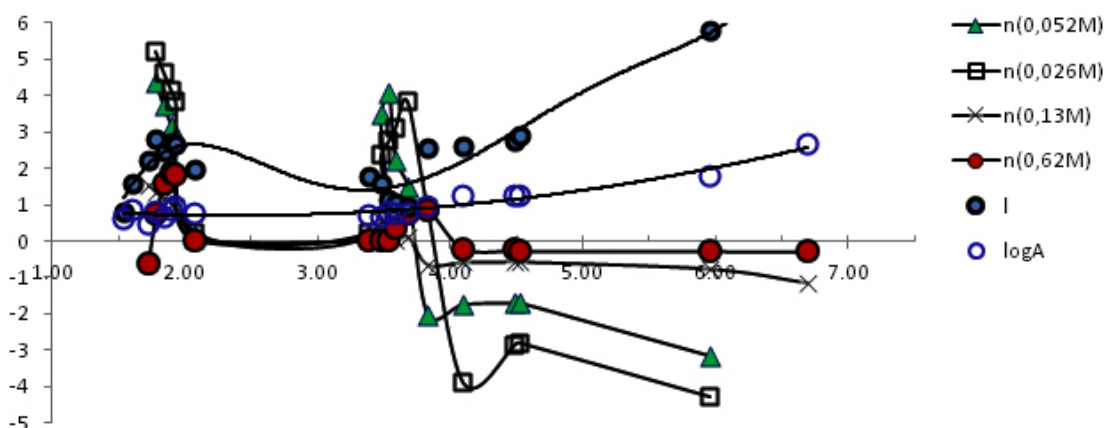


Fig.3: Variations of l, n, and A versus pH, obtained for H_3PO_4 2.5M, at $C_{LH} = 0.026, 0.052, 0.13$, and $0.62M$.

$$K_{l0} = \frac{[Cd(LH_2)_2L(X)]^{2+}}{[Cd^{2+}][LH_2^+X^-]^l} \quad \dots(5)$$

and

$$K_{ln} = \frac{[Cd(LH_2)_2L(X)]_l H_{-n}^{(2-n)+} [H^+]^n}{[Cd^{2+}][LH_2^+X^-]^l} \quad \dots(6)$$

Assuming in first approximation that

$$[\overline{Cd}] < C_{LH}, \text{ which results in } [LH_2^+X^-] = C_{LH}$$

we obtain:

$$\log D = \log K_{ln} + l \log C_{LH} + npH \quad \dots(7)$$

One can note that n=0 for ion-pair formation.

The nature of C_{in} extracted species noted thereafter (l, n) can be obtained from $\log D = f(\log C_{LH}; pH)$ variations according to modified slopes method:

$$\left(\frac{\partial \log D}{\partial pH}\right)_{C_{LH}} = n \quad \dots(8)$$

and

$$\left(\frac{\partial \log D}{\partial \log C_{LH}}\right)_{pH} = l \quad \dots(9)$$

The parameters n and l are varying with experimental conditions. As indicated above there is no predominant extraction reaction, that Cd extracted specie often results in combining two entities⁶⁻⁷. Conventional methods of slope analysis can't be performed successfully in this condition^{10; 13}. In this case numerical modeling procedure is performed by fitting experiment data to a polynomial equation]

Fig. 3 shows plots of $\left(\frac{\partial \log D}{\partial pH}\right)_{C_{LH}} = n$

and $\left(\frac{\partial \log D}{\partial \log C_{LH}}\right)_{pH} = l$ as a function of pH. As shown, the molar ratio metal: LH: H_3O^+ are varying continuously in extracted entities with aqueous solution acidity. Overall equilibrium

constant are obtained from the origin ordinates of $\log D = f(\log C_{LH})$ given by $A = \log K_{ln} + n pH$.

From these results the extraction reaction is found to be influenced by both extractant concentration and aqueous media acidity. The mechanism of this reaction involves deprotonation in more acidic condition ($pH < 2$) and for pH ranging from 3.4 to 4.1. Under mild acidic medium ($pH 2.2 - 3.3$) recovery proceeds entirely by no ion exchange, in all the cases, and also for $C_{LH} = 0.62$ M, at $pH > 4.1$. While in soft acidic conditions ($4.1 < pH < 7$), OH^- exchange is prevalent, for $C_{LH} = 0.026, 0.052$, and 0.13 M,

Evaluation of KI, n

Table I show, as example, some overall and predominant extraction constants.

It is interesting to indicate that l and %n% represent successively the ligand number involved in extracted specie, and the predominant H^+ or OH^- exchange reactions, contributing to overall equilibrium. Thus the overall constant of extracted complex (l, n), combining for successive (l', i), (l', j), and (l'', i), (l'', j) species is given by:

$$K_{l,n} = (K_{l',n})^{(1-x)}(K_{l'',n})^x \quad \dots(10)$$

With $l' < l < l''$, $l'' = l' + 1$, and $x = l - l'$,

$$\text{and } K_{l,n} = (K_{l',i})^{(1-y)}(K_{l',j})^y \quad \dots(11)$$

with $|i| < |n| < |j|$ and $|j| = |i| + 1$, and $y = |n| - |i|$ and $K_{l,i} = (K_{l',i})^{(1-x)}(K_{l'',i})^x \quad \dots(12)$

$$K_{l,j} = (K_{l',j})^{(1-x)}(K_{l'',j})^x \quad \dots(13)$$

$$K_{l,n} = (K_{l',i})^{(1-x)(1-y)}(K_{l',j})^{y(1-x)^2} (K_{l'',i})^{x(1-y)} (K_{l'',j})^{xy} \quad \dots(14)$$

This allows to obtain :

$$\log K_{l,n} = (1-x) (1-y) \log K_{l',j} + y(1-x) \log K_{l',i} + x(1-y) \log K_{l'',i} + x(y) \log K_{l'',j} \quad \dots(15)$$

As example, the overall partition equilibrium (2.68; 1.83) in the pH range 1.9 to 2, involves successive extracted species (2; 1), (2; 2), (3; 1), and (3; 2). Taking into account the protonation of amino group at $pH < 3^{6-7}$, and percentage distribution of phosphoric complexes of cadmium versus pH^{15} , predominant reactions combing, in this case, in overall extraction are as follows:

The equilibrium constants for the individual reactions could be obtained from the overall equilibrium constant K_{in} according to:

$$(1-x)(1-y)(\text{Cd}(\text{H}_2\text{PO}_4)_N^{(2-N)+} + \text{H}_3\text{PO}_4 + (2-l')(\overline{\text{LH}_2^+\text{X}^-}) + \text{H}_2\text{O} \\ \rightleftharpoons \overline{\text{Cd}(\text{H}_2\text{PO}_4)_N(\text{H}_3\text{PO}_4)_{2-N}\text{H}_{-(2-N)}\cdot 2(\overline{\text{LH}_2^+\text{X}^-})} + (1-i)\text{HO}_3^+; N=1: K_{21} \quad \dots(16)$$

$$(1-x)(y)(\text{Cd}(\text{H}_2\text{PO}_4)_N^{(2-N)+} + 2\text{H}_3\text{PO}_4 + (2-l')(\overline{\text{LH}_2^+\text{X}^-}) + 2\text{H}_2\text{O} \\ \rightleftharpoons \overline{\text{Cd}(\text{H}_3\text{PO}_4)_2\text{H}_{-2}\cdot 2(\overline{\text{LH}_2^+\text{X}^-})} + (2=i)\text{HO}_3^+; N=0: K_{22} \quad \dots(17)$$

$$(x)(1-y)(\text{Cd}(\text{H}_2\text{PO}_4)_N^{(2-N)+} + \text{H}_3\text{PO}_4 + (3-l'')(\overline{\text{LH}_2^+\text{X}^-}) + \text{H}_2\text{O} \\ \rightleftharpoons \overline{\text{Cd}(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)\text{H}_{-1}\cdot 3(\overline{\text{LH}_2^+\text{X}^-})} + (1=i)\text{HO}_3^+; N=1: K_{31} \quad \dots(18)$$

$$(x)(y)(\text{Cd}(\text{H}_2\text{PO}_4)_N^{(2-N)+} + 2\text{H}_3\text{PO}_4 + (3-l'')(\overline{\text{LH}_2^+\text{X}^-}) + 2\text{H}_2\text{O} \\ \rightleftharpoons \overline{\text{Cd}(\text{H}_3\text{PO}_4)_2\text{H}_{-2}\cdot 3(\overline{\text{LH}_2^+\text{X}^-})} + (2=j)\text{HO}_3^+; N=0: K_{32} \quad \dots(19)$$

$$(\text{Cd}(\text{H}_2\text{PO}_4)_N^{(2-N)+} + (2+x=l)(\overline{\text{LH}_2^+\text{X}^-}) + (n=1+y)\text{H}_3\text{PO}_4 + n\text{H}_2\text{O} \\ \rightleftharpoons \overline{\text{Cd}(\text{H}_2\text{PO}_4)_N(\text{H}_3\text{PO}_4)_n\text{H}_{-n}\cdot 2(\overline{\text{LH}_2^+\text{X}^-})} + (1+y=n)\text{HO}_3^+; N=0; 1: K_{in} \quad \dots(20)$$

The equilibrium constants for the individual reactions could be obtained from the overall equilibrium constant K_{in} according to:

$$K_{in} = (K_{21})^{(1-x)(1-y)} (K_{22})^{(1-x)(y)} (K_{31})^{(x)(1-y)} (K_{32})^{(x)(y)} \quad \dots(21)$$

and

$$\log K_{in} = (1-x)(1-y) \log K_{21} + (1-x)(y) \log K_{22} + (x)(1-y) \log K_{31} + (x)(y) \log K_{32} \quad \dots(22)$$

As example, in the case of (2.68; 1.83) complex we have:

$$\log K_{2.68,1.83} = (0.32)(0.17) \log K_{21} + (0.32)(0.83) \log K_{22} \\ + (0.68)(0.17) \log K_{31} + (0.68)(0.83) \log K_{32} \quad \dots(23)$$

CONCLUSION

3-methyl-2 (1H)- Methyl Quinoxaline-2-thione ($\overline{\text{LH}}$) is used for the extraction for cadmium from phosphoric acid (2.5 M). This extraction is varying with initial organic ligand concentration and pH. The stoichiometry of the extracted Cd(II) complex is varying between 1:1:0 and 1:3:3: Cd: $\overline{\text{LH}}$: H_3O^+ (OH).

This stoichiometry was determined by a modified slope analysis. The extraction reaction is a complex process including ion exchange-ion pair formation, organic and inorganic complexation, H_3PO_4 deprotonation and solvation phenomena. A best recovery of 43 to 60% is achieved in acidic conditions with $C_{\overline{\text{LH}}} = 0.26\text{M}$.

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