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ORIGINAL RESEARCH PAPER

POLY(AMINOMETHYLENEPHOSPHONIC) ACID FOR SOLVENT EXTRACTION OF METAL IONS

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Abstract: Diaminododecyltetramethylenetetraphosphonic acid (DADTMTPA) has been investigated in liquid - liquid extraction of Zn (II) and Cu (II) in acetate media. The extraction of both cations was carried out in different media with the addition of CH_3COONa, CH_3COOH, HCl and H_2SO_4 at different *p*H values. The maximum extraction yield for copper is 70% after addition of 10 mg of sodium acetate and for zinc is 30% after addition of acetic acid at $pH_i = 5.5$, in one step.

Keywords: *copper (II),* DADTMTPA*, solvent extraction, zinc (II), diaminododecyltetramethylenetetraphosphonic acid*

INTRODUCTION

Heavy metal contamination is an increasing worldwide environmental concern [1]. The main sources of heavy metals in the environment are industrial, agricultural and urban activities. Their presence in the nature (urban water and water of the industrial discharges), in the hydrocarbons and ores, rise to technological insurmountable problems until our days, in particular the processes of transformation. Zinc and copper are essential in various biological and enzymatic reactions [2]. However, their large concentrations in the environment can severely affect aquatic as well as human life [3, 4].

The synthesis of new organophosphorus extractants which form stable form complexes with metallic species is of great importance for improving existing hydrometallurgical processes for their recovery [5]. In fact, in this work, the used extractant, diaminododecyltetramethylenetetraphosphonic acid (DADTMTPA), was synthesized and characterized by the authors [6]. We have studied this new acid in the recovery of the two metal species Zn^{2+} and Cu^{2+} under the optimal conditions in different media, in one step.

EXPERIMENTAL

Reagents and solutions

The reagents used in the present work were zinc and copper acetates, purchased from Merck.

The aqueous solution concentrations of Zn^{2+} and Cu^{2+} in acetate medium were taken as 2 $mmol.L^{-1}$ and the extractant (DADTMTPA) solution concentrations ranged between 6.1 and 30 $mmol.L^{-1}$.

Instrumentation

A Phywe WTM 320 with combined glass electrode was used to measure the *p*H of the aqueous solution before and after extraction. In a water-acetone mixture (15:5), a known mass of the DADTMTPA was titrated with a solution of NaOH (5 $mmol.L^{-1}$). Metal ions were determined using the electrothermal atomic absorption GFAAS, system GBC 932, and system 3000 automated graphite furnace (GBC Scientific Equipment, Dandenong, Australia). Background correction was made with deuterium lamp and propylic graphite tubes were used.

Structure of DADTMTPA

The obtained pKa_i: 1.79, 2.3, 3.0 and 5.0 indicated that in water-acetone medium, the fourth acidity is not attained corresponding to very weak acidity.

The presence of P=O wide band indicates hydrogen intramolecular bonds P=O·····H–OP and N|·····>H–O–P. The DADTMTPA is soluble in most organic solvents, and shows intermolecular hydrogen bonding, forming polymers depending on the solvent polarity

[7]. Thus, in chloroform that we used in our study, the DADTMTPA is generally present in a dimeric form, as shown in Figure 1 [8, 9].

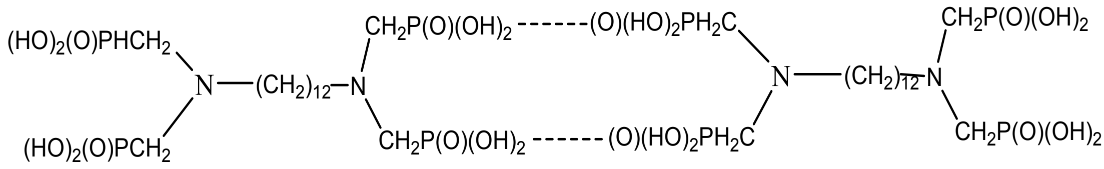

***Figure 1**. Dimeric form of DADTMTPA*

Extraction experiments

The extraction experiments were carried out with DADTMTPA dissolved in chloroform. After various preliminary tests with different solvents, chloroform has been chosen since it dissolves the extractant without trouble or emulsion.

The appropriate volume of the aqueous solution (10 mL) containing the metal ion and the DADTMTPA (aqueous/organic volume ratio of 3 : 1) were mixed in glass flasks. The mixtures were shaken in a moderate way, for at least 30 min for Zn^{2+} and 15 min for Cu^{2+}. All the experiments were carried out at 20 °C.

RESULTS AND DISCUSSION

The results of extraction experiments will be discussed in terms of distribution coefficient (*D*) and extraction yield (*Y*) [1].

Extraction kinetics

The equilibrium times were 30 min for Zn^{2+} and 15 min for Cu^{2+} because Zn^{2+} presented a mass transfer resistance more important compared to Cu^{2+} [10]. The results are shown in Figure 2.

Effect of reagent concentration on the extraction of copper and zinc in neutral media

The results of the extraction of Zn^{2+} and Cu^{2+} in neutral media at *p*H 6.4 to 6.8, from 2 mmol.L^{-1}, function of the ligand-to-cation ratio *Q*, are shown in Figure 3. The extractant concentrations varies from 6.1 to 30 mmol.L^{-1} (Q = 1 to 5). We reached an extraction yield of 23% for zinc and 44 % for copper (Figure 3).

The yield of extraction increases with *Q*. The extraction with a longer alkyl group forms more hydrophobic complexes. The hydrophobic character of the ligand can be determined calculating log *P* which is defined as the partition coefficient of a substance between two phases, generally *n*-octanol and water. Modern molecular modeling software allows the log *P* value to be easily calculated. The *C* log *P* value, calculated using ChemDraw (Cambridge Soft) is 1.745 for DADTMTPA showing that is strongly hydrophobic.

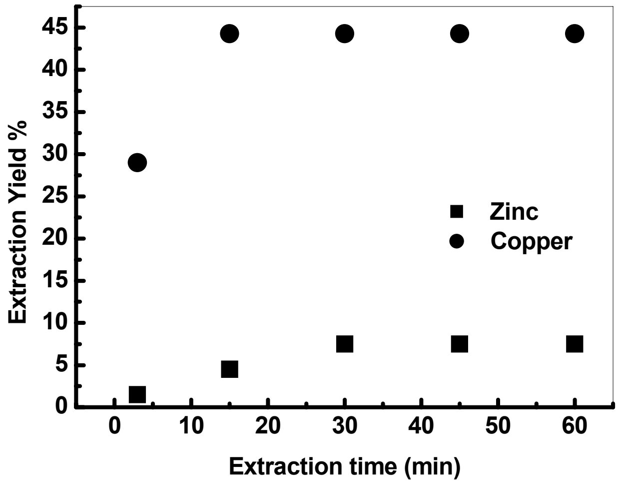

Figure 2. *Extraction kinetics of Zn^{2+} and Cu^{2+}*
[DADTMTPA] = 6.15×10^{-3} M, $[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}
$Q = 1$, $V_{aq}/V_{org} = 3$, $T = 20$ °C

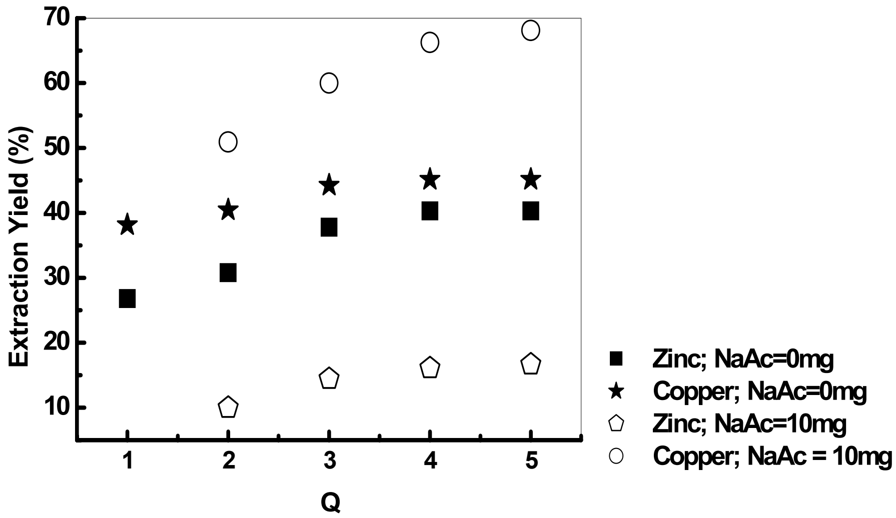

Figure 3. *Effects of molar ratio on the extraction yield, with and without salt addition*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $m_{NaAc} = 10$ mg, $V_{aq}/V_{org} = 3$, $T = 20$°C

Zn^{2+} and Cu^{2+} possess an octahedral structure in aqueous phase; their extraction gives complexes of a tetrahedral structure in organic solvents as reported in literature [11].
The stoichiometric coefficients obtained from the plots ln D vs ln [DADTMTPA] and ln D vs $p\mathrm{H}_{eq}$, shown in Figures 4 and 5 respectively, may suggest the reaction mechanism in neutral media.
This result led us to propose the following extraction equilibrium:

$$2\,Cu^{2+} + 4\overline{(H_8A)}_2 \leftrightarrow \overline{[\,Cu\cdot(H_6A)\cdot(H_8A)_2\,]_2} + 4H^+ \quad (1)$$

$$2\,Zn^{2+} + (\overline{H_8A})_2 \leftrightarrow \overline{[Zn\cdot H_6A]_2} + 4H^+ \quad (2)$$

In this case, the metal complexes formed in the organic phase, $[Cu\cdot(H_6A\cdot H_8A)_2]_2$ and $[Zn\cdot H_6A]_2$, are not identical in neutral media. The two acidities used in our extraction correspond to the pK_a 1.79 and 2.3 of the acidic DADTMTPA.

The DADTMTPA extracts in cationic exchange mode with substantial yields because the extractions are done to only one cycle.

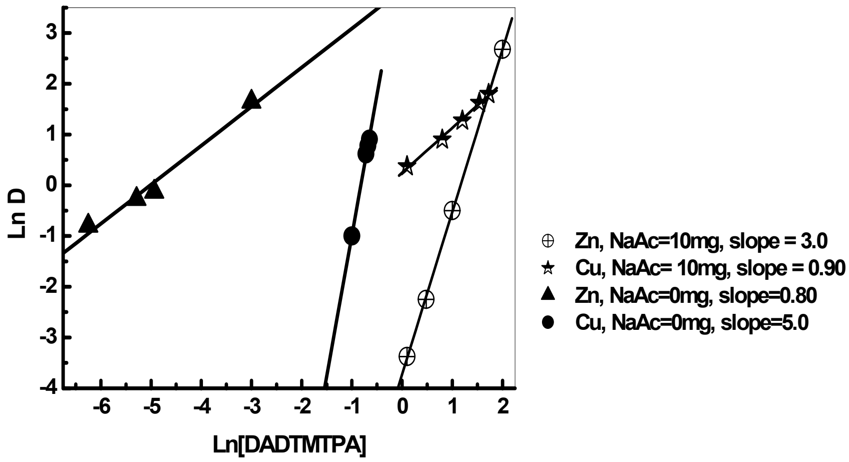

Figure 4. *Effect of the extractant concentration on the distribution ratio; extraction after the addition 10 mg of sodium acetate* $[Zn^{2+}] = [Cu^{2+}] = 2\ mmol.L^{-1}$, $V_{aq}/V_{org} = 3$, $T = 20\ °C$

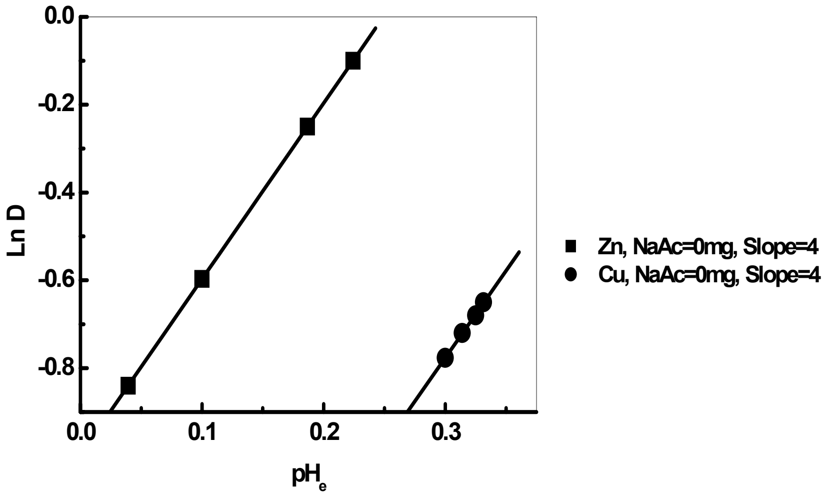

Figure 5. *Effect of equilibrium pH on the distribution ratio for* Zn^{2+} *and* Cu^{2+} $[Zn^{2+}] = [Cu^{2+}] = 2.10^{-3}\ M$, $V_{aq}/V_{org} = 3$, $T = 20\ °C$

Influence of the ionic strength on the extraction of copper and zinc

The influence of the ionic strength on the extraction yield, has been studied adding to the aqueous phase sodium acetate. The sodium acetate concentrations are taken equal to 0.014 M (10 mg.L^{-1}), 0.11 M (80 mg.L^{-1}) and 1.0 M (738 mg.L^{-1}). The operating conditions are fixed like previously. The growth of the optimal extraction yield of 70% for Cu^{2+} was obtained after adding 10 mg of sodium acetate, whereas for Zn^{2+}, the yield decreased to 18%. This is assigned to the common ion effect that lowers the solubility of the zinc salt. Figure 3 shows that the extraction yield of Cu^{2+} is better than that of Zn^{2+}. With such an amount, the extraction of Zn^{2+} enters in competition with sodium. The Na^{+} is extracted instead of Zn^{2+}. The formed complex in the organic phase is $Na{\cdot}H_7A{\cdot}H_8A$ [12].
The addition of the sodium acetate decreases the extraction yield of zinc whatever the added quantity of sodium acetate [7]. However, the best yield is obtained after the addition of 10 mg of sodium acetate. The extraction of copper is improved whatever is the added quantity of sodium acetate, and the extraction yield reaches 70% with the addition of the weakest ionic strength of 10 mg of sodium acetate.
Stoichiometric coefficients for the extraction reactions mechanisms of Zn^{2+} and Cu^{2+} are determined from the plots presented in Figures 4 and 6. This result led us to suggest the following extraction equilibria:

$$2Cu^{2+} + \overline{(H_8A)_2} \leftrightarrow \overline{[Cu{\cdot}(H_6A)]_2} + 4H^{+} \quad (3)$$

$$2\,Zn^{2+} + Na^{+} + 3\overline{(H_8A)_2} \leftrightarrow \overline{[Zn{\cdot}(H_6A){\cdot}(H_8A)]_2} + \overline{Na{\cdot}(H_7A){\cdot}(H_8A)} + 5H^{+} \quad (4)$$

The dimerized complex of zinc with DADTMTPA is $[Zn{\cdot}(H_6A){\cdot}(H_8A)]_2$ and that of copper is $[Cu{\cdot}(H_6A)]_2$ [13].

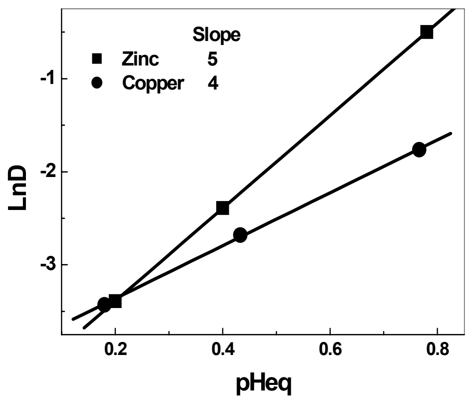

Figure 6. *Effect of the equilibrium pH on the distribution ratio of Zn^{2+} and Cu^{2+} after addition of 10 mg of sodium acetate*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$, T = 20 °C

Effect of acid media on the extraction of copper and zinc

The extraction of Cu^{2+} and Zn^{2+} has been achieved from aqueous solutions in acidic media at *p*H = 3, *p*H = 4 and *p*H = 5.5, adjusted with adequate quantities of acid (acetic, hydrochloric, sulfuric) to each solution with a micropipette.

Acetic acid addition influence

In order to verify the influence of the addition of an acetate anion in the aqueous phase on the extraction yield, we added acetic acid.
Figure 7 shows that acetic acid addition slightly improves the extraction of Zn^{2+} for $Q \leq 3$, whatever the pH of the solution. It is the effect of H^+ that predominates, while for $Q > 4$, it is the effect of the acetate which predominates. In the range $3 < Q < 4$, both effects take place. For Cu^{2+} (Figure 7) the acetic acid addition increases the extraction yield. It reaches 50% at $pH_i = 4$.

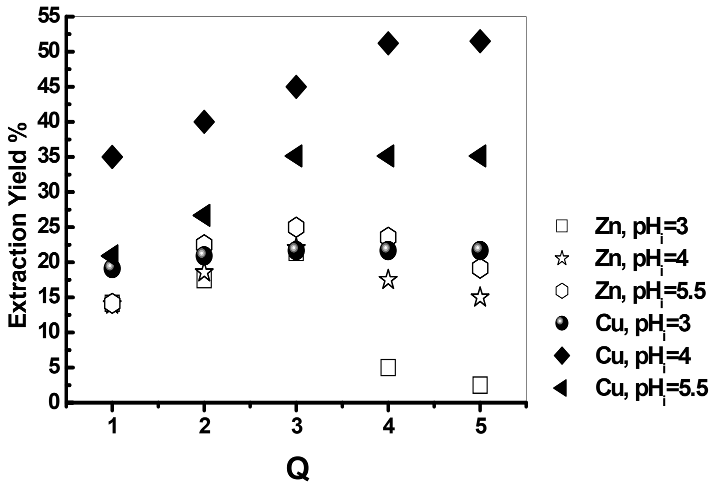

Figure 7. *Effect of molar ratio on the extraction yield of Zn^{2+} and Cu^{2+} in acetic acid medium: $[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$, equilibrium time = 30 min for Zn, equilibrium time = 15 min for Cu*

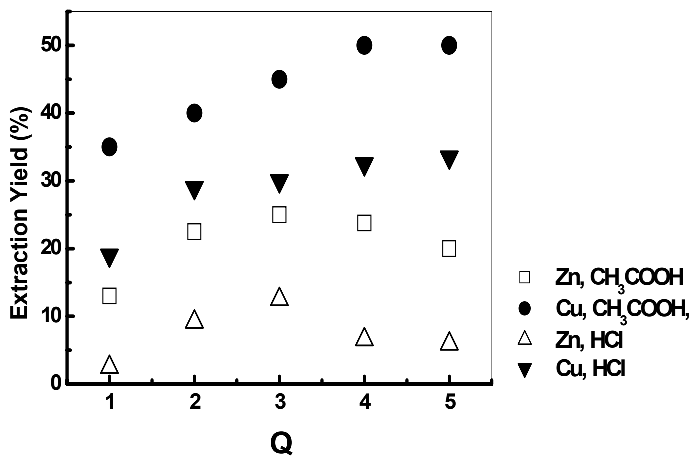

Figure 8. *Effect of molar ratio on the extraction yield of Zn^{2+} and Cu^{2+} after addition of acetic acid then addition of hydrochloric acid at $pH_i = 5.5$ $[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$,*

Stoichiometric coefficients are determined from plots shown in Figures 9 and 10 allowing us to propose the following equations of the extraction equilibrium:

$$Cu^{2+} + 2H^{+} + 1/2\overline{(H_8A)_2} \leftrightarrow \overline{Cu{\cdot}H_6A} + 4H^{+} \tag{5}$$

$$Zn^{2+} + 3H^{+} + \overline{(H_8A)_2} \leftrightarrow \overline{Zn{\cdot}H_6A{\cdot}H_8A} + 5H^{+} \tag{6}$$

Acetic acid protons compete with the two metal cations in the extraction process.
The formula of the complex of zinc with the DADTMTPA is in dimeric form, $Zn{\cdot}H_6A{\cdot}H_8A$, meanwhile that of copper is in monomeric form, $Cu{\cdot}H_6A$.

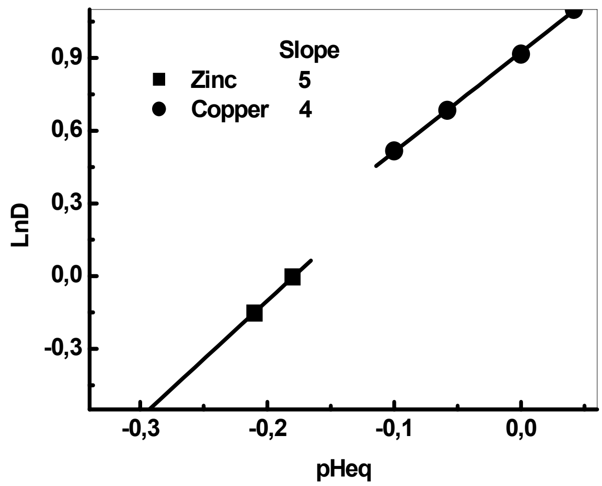

Figure 9. *Effect of equilibrium pH on the distribution ratio of Zn^{2+} and Cu^{2+} after addition of acetic acid*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$

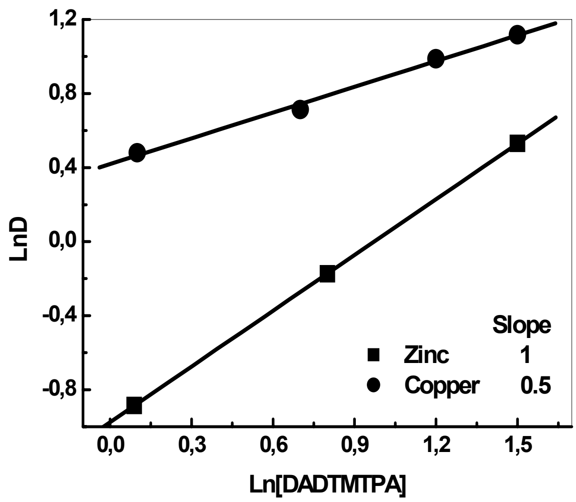

Figure 10. *Effect of extractant concentration on the distribution ratio of Zn^{2+} and Cu^{2+} after addition of acetic acid*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$

Hydrochloric acid addition influence

Figure 11 shows that the extraction yield of Zn^{2+} decreases significantly whatever the value of the *p*H. However, for Cu^{2+} the yield obtained was 33% at $pH_i = 5.5$.

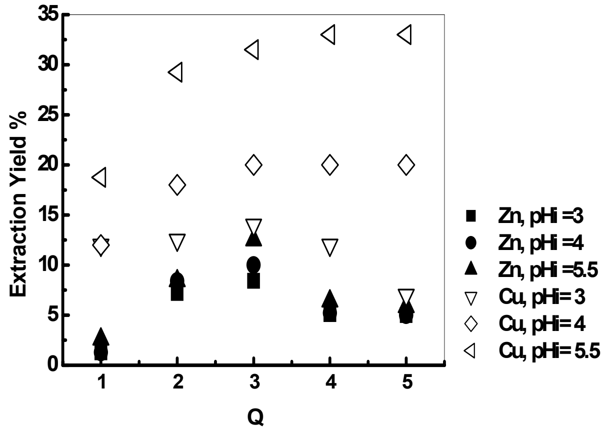

***Figure 11**. Effect of molar ratio on the extraction yield of Zn^{2+} and Cu^{2+} in hydrochloric acid medium*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$, T = 20 °C
equilibrium time = 30 min for Zn, equilibrium time = 15 min for Cu

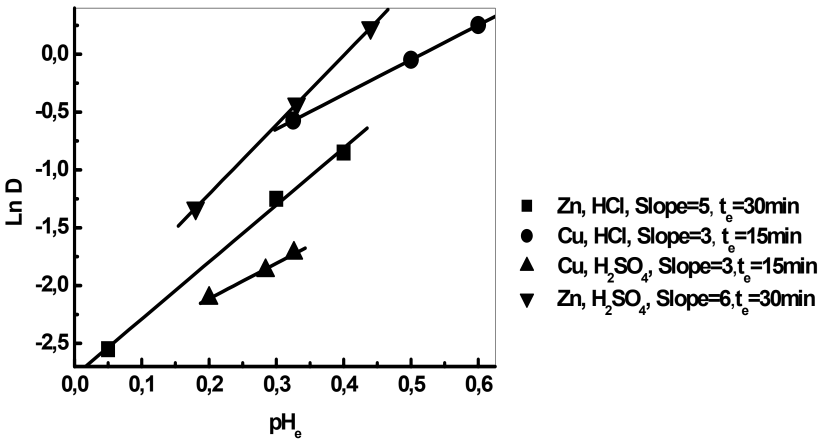

***Figure 12**. Effect of equilibrium pH on the distribution ratio of Zn^{2+} and Cu^{2+}after addition of hydrochloric acid, then addition of sulphuric acid at pH_i=5.5*
$[Zn^{2+}] = [Cu^{2+}] = 2$ mmol.L^{-1}, $V_{aq}/V_{org} = 3$, T = 20 °C

Figures 12 and 13 let us to suggest the following equilibrium extraction equations:

$$Cu^{2+} + H^+ + \overline{(H_8A)_2} \leftrightarrow \overline{Cu{\cdot}H_6A{\cdot}H_8A} + 3H^+ \quad (7)$$

$$Zn^{2+} + 3H^+ + 2\overline{(H_8A)_2} \leftrightarrow \overline{Zn{\cdot}H_6A{\cdot}H_8A} + 5\,H^+ \quad (8)$$

Hydrochloric acid protons compete with the two metal cations in the extraction process. The structure of the zinc complex is $Zn \cdot H_6A \cdot H_8A$,, similar with those of copper, $Cu \cdot H_6A \cdot H_8A$.

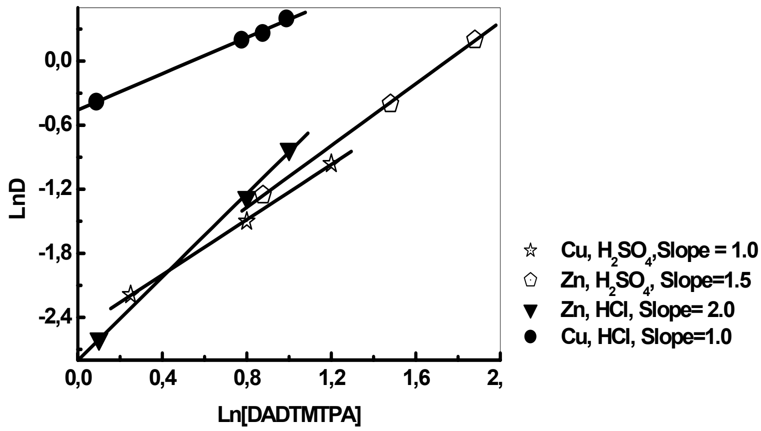

Figure 13. *Effect of extractant concentration on the distribution ratio of* Zn^{2+} *and* Cu^{2+} *after addition of hydrochloric acid then addition of sulphuric acid at pH=5.5*
$[Zn^{2+}] = [Cu^{2+}] = 2\ mmol.L^{-1}$, $V_{aq}/V_{org} = 3$, $T = 20\ °C$

Sulphuric acid addition influence

From Figures 12 and 13, the slopes 1.5 and 6 for zinc and 1 and 3 for copper respectively as stoichiometric coefficients for the ligand and *p*H lead us to suggest the following equations:

$$Cu^{2+} + H^+ + CuHSO_4^+ + \overline{(H_8A)_2} \leftrightarrow \overline{Cu \cdot H_6A} + \overline{CuHSO_4 \cdot H_7A} + 3H^+ \quad (9)$$

$$Zn^{2+} + ZnHSO_4^+ + 3H^+ + 1.5\overline{(H_8A)_2} \leftrightarrow \overline{Zn \cdot H_6A \cdot H_8A} + \overline{ZnHSO_4 \cdot H_7A} + 6\,H^+ \quad (10)$$

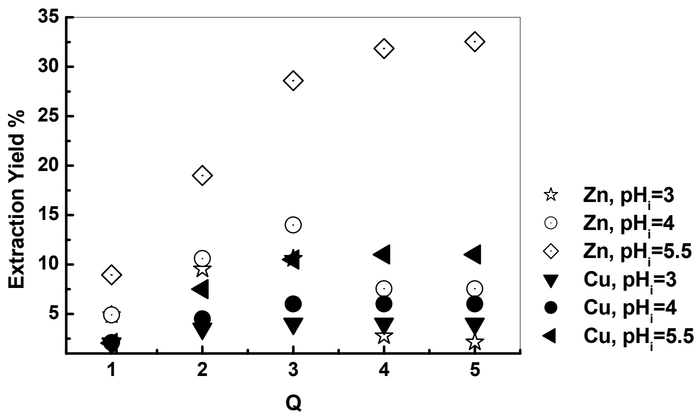

Figure 14. *Effect of molar ratio on the extraction yield of* Zn^{2+} *and* Cu^{2+} *in sulphuric acid medium*
$[Zn^{2+}] = [Cu^{2+}] = 2\ mmol.L^{-1}$, $V_{aq}/V_{org} = 3$, $T = 20\ °C$
equilibrium time = 30 min for Zn, equilibrium time = 15 min for Cu

The structure of the complex of zinc is $Zn{\cdot}H_6A{\cdot}H_8A$, different from that of copper, $Cu{\cdot}H_6A$. The complexes thus formed, $ZnHSO_4{\cdot}H_7A$ and $CuHSO_4{\cdot}H_7A$, can be explained by the fact that the sulfate anion itself forms very stable complexes with Zn^{2+} and Cu^{2+}. Therefore the sulfate anion competes with the anion of the ligand DADTMTPA for the coordination sites.
From the three acids, for Zn^{2+} at $pH_i = 5.5$ and $Q = 5$, sulfuric acid is the best medium with the best extraction yield (33.5%), Figure 14. For Cu^{2+} at $pH_i = 4$ and $Q = 5$, acetic acid is the best medium with the best extraction yield (53%).

CONCLUSIONS

The solvent extraction of the species Cu (II) and Zn (II) with DADTMTPA dissolved in chloroform was explained taking into account the formation of different complexes.
In acetate medium, the extraction kinetics are slower for Zn (II) than Cu (II). The optimal extraction parameters for both metal ions concentration of 2 mmol.L^{-1} in the aqueous phase and 24 mmol.L^{-1} in the organic phase, are $Q = 4$, $V_{aq}/V_{org} = 3$, $T = 20$ °C. The last four values of pK_a obtained by potentiometric measurement confirm that the extracting agent can exchange two protons per molecule.
In neutral media, $[Cu{\cdot}(H_6A{\cdot}H_8A)_2]_2$ and $[Zn{\cdot}H_6A]_2$ are the complexes formed in the organic phase. In the presence of 10 mg of sodium acetate in the aqueous phase, 70 % of Cu (II) can be extracted, whereas Zn (II) is extracted only 18%. The metal complexes formed in the organic phase are $[Cu{\cdot}H_6A]_2$ and $[Zn{\cdot}H_6A{\cdot}H_8A]_2$. In acetic acid medium, the extraction yield obtained is 50% for Cu (II) and 29% for Zn (II) at $pH_i = 5.5$ respectively. The complexes formed in the organic phase are $Zn{\cdot}H_6A{\cdot}H_8A$ and $Cu{\cdot}H_6A$. The extraction yield is 33% for Cu (II) and only 12% for Zn (II) and the metal complexes formed are $Zn{\cdot}H_6A{\cdot}H_8A$ and $Cu{\cdot}H_6A{\cdot}H_8A$ in hydrochloric acid medium. For Zn (II), the maximum extraction obtained is 30% in sulfuric acid medium at $pH_i = 5.5$ but for Cu (II) is only 12% and the formed metal complexes are $Cu{\cdot}H_6A$, $CuHSO_4{\cdot}H_7A$, $Zn{\cdot}H_6A{\cdot}H_8A$ and $ZnHSO_4{\cdot}H_7A$.

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