A Rigorous Calculation Method for Determining Potential-pH Diagrams Part I: Copper in Aqueous Solutions of Various Complexing Agents

Ramdane Salhi+*

Department of Chemistry, Faculty of Sciences, University of Mentouri Constantine, ALGERIA

ABSTRACT: *The main aim of this research is to determine optimal leaching conditions; Eh, pH and complexing agent concentrations, for recovery of Copper from hydroxide sludges such as those produced by electroplating shops, metal finishers, treatment of acid mine drainage, and industrial wastewater in general. This has been preceded by a theoretical approach and numerical and computer calculation. Potential-pH diagrams for the copper-water-ammonia, copper-water-cyanide, copper-water-glycine, copper-water-ethylenediamine (En) and copper-water-ethylene-diaminetetraacetic acid (EDTA) systems are derived at different total copper and complexing agent concentrations. The originality of our method is the introduction of a rigorous calculating method; we don't neglect any equilibrium or species for Eh-pH diagrams and with the free concentration of complexing agent (pL-pH) diagram to show the stable regions of soluble copper species.*

KEY WORDS: *Computational chemistry, Copper, Leaching, Industrial waste.*

INTRODUCTION

There are several potential applications for complexing agents in mineral and metallurgical processing operations. In some cases these agents may provide excellent lixiviant action, while being environmentally benign. Several studies have investigated the potential of ammonia as lixiviant. These include the leaching of copper and nickel from electroplating hydroxide sludges [1, 2], metal finishers, treatment of acid mine drainage, and industrial wastewater in general [3], roast reduced deep-sea manganese nodules [4], *Jeffrey* use ammonia-thiosulfate solutions as lixiviants for gold and silver [5]. *Guan* uses the cyanide as lixiviants for gold-silver alloys

[6]. *Philip* has suggested the use of ammoniacal thiosulfate and sodium cyanide as lixiviants for preg-robbing Goldstrike ore carbonaceous matter [7]. *Han* use halogen salts as lixiviants for precious metals from secondary sources [8]. *Feng* has developed the ammonical thiosulphate leaching for gold-host sulphides such as chalcopyrite, pyrite, arsenopyrite and pyrrhotite [9]. *Peters* has suggested the use of organic amines, such as ethylenediamine (En), as lixiviants for lead sulfate ores [10]. Several studies have investigated the potential of ethylenediaminetetraacetic acid (EDTA) as a chelating lixiviant. These include the leaching of nickel from low-

grade lateritic ores [11], the leaching of copper from carbonate-silicate ores [12], covellite [13], malachite [14], and chalcocite [15], the leaching of boron from colemanite ores [16] and the leaching of tungsten from scheelite ores [17].

The construction of Eh-pH diagrams is a useful way to summarize redox properties and chemical speciation. This diagram shows the Eh-pH domains for a number of aqueous systems. The most well known of such stability or predominance area diagrams is the Eh-pH diagram introduced by *Pourbaix* [18]. Eh-pH diagrams enable us to see at a glance the range of stability of aqueous species and solid compounds under specified conditions of Eh (or redox potential) and pH.

A side from Eh-pH diagrams, other predominance area diagrams of interest include log [M]-pH and log [Ligand]-pH diagrams. In this work the thermodynamic basis and the mathematical formalism underlying the construction of predominance area diagrams are developed. These thermodynamic and mathematical concepts are then applied to complex systems such as those of the type Metal-Ligand-H_2O.

In this paper, we present potential-pH diagrams for the copper - water - ammonia, copper - water - cyanide, copper-water-glycine, copper-water-En and copper water-EDTA systems at different total copper and complexing agent concentrations.

THEORETICAL

In hydrometallurgical systems, when en a concentrated solution is considered, it is preferable to use concentration constants rather than activity constants [19].

$\left[L^m\right]_T^{Cu(I)}$: Is the concentration of total ligand in solution of Copper (I) ions

$\left[L^m\right]_T^{Cu(II)}$: Is the concentration of total ligand in solution of Copper (II) ions

$\left[L^m\right]_L^{Cu(I)}$: Is the concentration of free ligand in solution of Copper (I) ions

$\left[L^m\right]_L^{Cu(II)}$: Is the concentration of free ligand in solution of Copper (II) ions

Where m denotes the charge of ligand L

$[Cu^+]_T$: Is the concentration of total Copper (I) ions

$[Cu^+]_L$: Is the concentration of free Copper (I) ions

$[Cu(L)_i^{(1-m)}]$: Is the concentration of complexes Copper (I) ions

$[Cu^{2+}]_T$: Is the concentration of total Copper (II) ions

$[Cu^{2+}]_L$: Is the concentration of free Copper (II) ions

$[Cu(L)_i^{(2-m)}]$: Is the concentration of complexes Copper (II) ions

$[Cu]_T$: Is the concentration of total Copper (II) and Copper (I) ions

K_{LHj}: Is the stability constants for protolytic reactions of ligand

K_{MLi}: Is the stability constants for Copper (II)-ligand reaction complexes

B_{MLi}: Is the stability constants for Copper (I)-ligand reaction complexes

K_{Dh}: Is the stability constants for Copper (II)- hydro-complexes

K_{s1}: Is the hydroxide solubility products for Copper (I) hydroxide

K_{s2}: Is the hydroxide solubility products for Copper (II) hydroxide

K_w: Is the ionic product of water

$pL = -Log[L]_L$

In metal finishing hydroxide sludges, the metal are usually present as hydroxides: $M(OH)_n$. The solubility's of $M(OH)_n$ in water are principally based on the expression for the solubility product K_s. The solubility affected by side reactions can be calculated by means of total concentration of metal ions as a function of pH at various values of total ligand, and redox potential can be calculated as a function of pH at various values of total concentration of metal and at various values of total concentration of ligand.

Various species of an element, which make up the total concentration of that element.

$[Cu^+]_T = f(pH, [L]_T = y)$ with, $pL = f(pH, [L]_T = y)$

$[Cu^{2+}]_T = f(pH, [L]_T = y)$ with, $pL = f(pH, [L]_T = y)$

$E = f (pH, [Cu]_T = x, [L]_T = y)$, with $pL = f (pH, [Cu]_T = x, [L]_T = y)$

Where

x: various values of total concentration of metal.

y: various values of total concentration of ligand.

Species present in solution and minerals to be considered:

- Solution: Cu^{2+}, Cu^+, $Cu(OH)^+$, $Cu(OH)_2$, $HCuO_2^-$, CuO_2^{2-}.

- Solids: Cu, CuO, Cu_2O.

For determining Cu_2O solubility, the following forms were taken into account: Cu^+ and $Cu(L)_i^{(1-m)}$, where i denotes the aqueous species complexed with the ligands and (1-m) is the charge of soluble species i.

For determining CuO solubility, the following forms were taken into account: Cu^{2+}, $Cu(OH)^+$, $Cu(OH)_2$, $HCuO_2^-$, CuO_2^{2-} and $Cu(L)_i^{(2-m)}$, where i denotes the aqueous species complexed with the ligands and (2-m) is the charge of soluble species i.

EQUILIBRIUMS AND EQUATIONS

a - Copper(I) hydroxide solubility (Cu₂O)

Conservation of the total concentration of ligand: $[L^m]_T^{Cu(I)}$

$$[L^m]_T^{Cu(I)} = [L^m]_L + \sum_{j=1}^{P}[H_j L^{K+}] + \sum_{i=1}^{n1} i[Cu(L)_i^{(1-m)}]^i \quad (1)$$

$$[L^m]_T^{Cu(I)} = [L^m]_L \left(1 + \sum_{j=1}^{P} \frac{[H^+]^j}{K_{LHj}}\right) + \quad (2)$$

$$[Cu^+]_L \left(1 + \sum_{j=1}^{nl} \frac{i[L^m]^i}{K_{Di}}\right)$$

$$[L^m]_T^{Cu(I)} = \alpha [Cu^+]_L \cdot \beta_1 \quad (3)$$

Where:

$$\alpha = [L^m]_L \left(1 + \sum_{j=1}^{P} \frac{[H^+]^j}{K_{LHj}}\right) \quad (4)$$

and

$$\beta_1 = [Cu^+]_L \left(1 + \sum_{i=1}^{nl} i[Cu(L)_i^{(1-m)}]^j\right) \quad (5)$$

Conservation of the total concentration of dissolved metal: $[Cu^+]_T$

$$[Cu^+]_T = [Cu^+]_L + \sum_{i=1}^{nl} [Cu(L)_i^{(1-m)}]^i \quad (6)$$

$$[Cu^+]_T = [Cu^+]_L \left(1 + \sum_{i=1}^{nl} \frac{i[L^m]^i}{K_{Di}}\right) \quad (7)$$

$$[Cu^+]_T = [Cu^+]_L \cdot \lambda_1 \quad (8)$$

Where:

$$\lambda_1 = 1 + \sum_{i=1}^{n} 10^{pK_{Di} - i \cdot pL} \quad (9)$$

b - Copper(II) hydroxide solubility (CuO)

Conservation of the total concentration of Ligand: $[L^m]_T^{Cu(II)}$

$$[L^m]_T^{Cu(II)} = [L^m]_L + \sum_{j=1}^{m}[H_j L^{k+}] + \sum_{i=1}^{n2} i[Cu(L)_i^{(2-m)}]^i \quad (10)$$

$$[L^m]_T^{Cu(II)} = [L^m]_L^2 \left(1 + \sum_{j=1}^{m} \frac{[H^+]^j}{K_{LHj}}\right) + \quad (11)$$

$$[Cu^{2+}]_L \left(1 + \sum_{i=1}^{n2} \frac{i[L^m]^i}{K_{Di}}\right)$$

$$[L^m]_T^{Cu(II)} = \alpha + [Cu^{2+}]_L \cdot \beta_2 \quad (12)$$

Where:

$$\beta_2 = [Cu^{2+}]_L \left(1 + \sum_{i=1}^{n2} i[Cu(L)_i^{(2-m)}]^i\right) \quad (13)$$

Conservation of the total concentration of dissolved metal: $[Cu^{2+}]_T$

$$[Cu^{2+}]_T = [Cu^{2+}]_L + [Cu(OH)^+] + \quad (14)$$

$$[Cu(OH)_2] + [Cu(OH)_3^-] + [Cu(OH)_4^{2-}] +$$

$$\sum_{i=1}^{n2} [Cu(L)_i^{(2-m)}]^i$$

$$[Cu^{2+}]_T = [Cu^{2+}]_T + \left(1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \quad (15)\right.$$

$$\left. \frac{K_3}{[H^+]^3} + \frac{K_4}{[H^+]^4} + \sum_{i=1}^{n2} \frac{[L^m]^i}{K_{Di}}\right)$$

$$\left[Cu^{2+}\right]_T = \left[Cu^{2+}\right]_L \cdot \lambda_2 \tag{16}$$

Where:

$$\lambda_2 = 1 + 10^{pH-796} + 10^{2pH-1624} + 10^{3pH-26869} + \tag{17}$$

$$10^{4pH-3999} + \sum_{i=l}^{n2} 10^{pK_{Di}-i \cdot pL}$$

and in solution of mixture: Cu^+ and Cu^{2+}

$$\left[L^m\right]_T = \alpha + \left[Cu^+\right]_L \cdot \beta_1 + \left[Cu^{2+}\right]_L \cdot \beta_2 \tag{18}$$

$\left[L^m\right]_T$: Is the concentration of total ligand in solution of mixture: Copper (I) and Copper (II) ions.

The Resulting Equation

We present our rigorous method; the system Copper-H_2O-ligand is described by our system of equation:

Different oxidation states of copper: 0, +1, +2

In system Copper-H_2O-ligand we calculated:

$$Cu^{2+} + e^- \Leftrightarrow Cu^+ \quad , \tag{19}$$

$$E_{21} = E_{21}^0 + 2.303 \frac{RT}{nF} \log \frac{\left[Cu^{2+}\right]}{\left[Cu^+\right]}$$

$$Cu^{2+} + e^- \Leftrightarrow Cu \quad , \tag{20}$$

$$E_{10} = E_{10}^0 + 2.303 \frac{RT}{nF} \log \left[Cu^+\right]$$

$$Cu^{2+} + 2e^- \Leftrightarrow Cu \quad , \tag{21}$$

$$E_{10} = E_{10}^0 + 2.303 \frac{RT}{nF} \log \left[Cu^+\right]$$

- If there are formation of precipitates Cu_2O and CuO, the free concentration of dissolved copper can be rigorously written:

$$\left[Cu^+\right]_L = 10^{pK_c - pK_a - pH} \tag{22a}$$

$$\left[Cu^+\right]_L = 10^{2pK_c - pK_a - 2pH} \tag{22b}$$

- If there are not formation of precipitates Cu_2O and CuO, the free concentration of dissolved metal can be rigorously written:

$$\left[Cu^+\right]_L = \frac{\left[Cu\right]_T}{\lambda_1} \tag{23a}$$

$$\left[Cu^{2+}\right]_L = \frac{\left[Cu\right]_T}{\lambda_2} \tag{23b}$$

and E^o, R, T, and F are the standard equilibrium electrochemical potential, gas constant, absolute temperature and Faraday's constant, respectively.

At 25 °C: $E_{21}^0 = 0.15$, $E_{10}^0 = 0.69$, $E_{20}^0 = 0.34$ volts, $pK_e = 14$, $pK_s(Cu_2O) = 14.84$, $pK_s (CuO) = 20.11$ [18].

Construction of Diagrams

This section summarizes the principles used to construct the solubility curves and potential-pH diagrams:

- The solubility curves and pL-pH diagrams are conventionally plotted with pH on the horizontal axis, solubility on the left vertical axis and pL on the right vertical axis.

- The potential-pH diagrams and pL-pH diagrams are conventionally plotted with pH on the horizontal axis, potential on the left vertical axis and pL on the right vertical axis.

The principal influence of pH and ligands on the solubility of copper from their hydroxides as a result of ligands complexation, the principal influence of pH, concentration of copper and ligands on Eh is shown in the followed theoretical diagrams.

Numerical Calculations and Computations

The results of calculation and computations are presented in the following figures, the used language is FORTRAN 77.

Copper-Water-Ammonia System

L=NH$_3$, m=0, p=1, n1=2, n 2=4

Ammonia exists in aqueous solutions in two different forms, namely NH_4^+ (ammonium), and NH_3 (ammonia). These species are denoted as HL^+ and L, respectively, in this paper. Ammonia forms soluble complexes with both cupric and cuprous ions.

The principal copper (II) ammonia complexes are $Cu(NH_3)^{2+}$, $Cu(NH_3)_2^{2+}$, $Cu(NH_3)_3^{2+}$ and $Cu(NH_3)_4^{2+}$, while the principal Cu(I) species is $Cu(NH_3)^+$, $Cu(NH_3)_2^+$. These are referred to as CuL^{2+}, CuL_2^{2+}, CuL_3^{2+}, CuL_4^{2+}, CuL^+ and CuL_2^+, respectively, in the following discussion.

Table 1 gives the association constants for ammonia and copper-ammonia species, at 25 ^{o}C [20], Fig. 1 shows log $[Cu^+]$-pH for 10^{-1} mol l^{-1} total ammonia concentration, Fig. 2 shows log $[Cu^{2+}]$-pH for 10^{-1} mol l^{-1} total ammonia concentration and Fig. 3 and Fig. 4 shows potential-pH diagrams for 10^{-1} mol l^{-1} total ammonia concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration, for 10^{-2} mol l^{-1} total ammonia concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

Copper-Water-Cyanide System

$L^- = CN^-$, m = -1, p = 1, n1 = 3, n2 = 1

Cyanide exists in aqueous solutions in two different forms, namely HCN (cyanide acid) and CN^- (anion). These species are denoted as HL and L^-, respectively, in this paper. Cyanide forms soluble complexes with both cupric and cuprous ions. The principal copper (II) cyanide complexes are $Cu(CN)_4^{2-}$, while the principal Cu(I) species is $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. These are referred to as CuL_4^{2-}, CuL_2^-, CuL_3^{2-} and CuL_4^{3-}, respectively, in the following discussion. Table 2 gives the association constants for cyanide and copper-cyanide species at 25 °C [18, 21], Fig. 5 shows log $[Cu^+]$-pH for 10^{-1} mol l^{-1} total cyanide concentration, Fig. 6 shows log $[Cu^{2+}]$-pH for 10^{-1} mol l^{-1} total cyanide concentration and Fig. 7 and Fig. 8 shows potential-pH diagrams for 10^{-1} mol l^{-1} total cyanide concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration, for 10^{-2} mol l^{-1} total cyanide concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

Copper-Water-Glycine System

$L^- = H2NCH2COO^-$, m = -1, p = 2, n1 = 1, n 2 = 3

Glycine is an amino acid that can exist in aqueous solutions in three different forms, namely $^+H_3NCH_2COOH$ (cation), $^+H_3NCH_2COO^-$ (zwitterion) and $H_2NCH_2COO^-$ (anion). These species are denoted as H_2L^+, HL and L^-, respectively, in this paper. Glycine forms soluble complexes with both cupric and cuprous ions. The principal copper (II) glycinate complexes are $Cu(H_3NCH_2COO)^{2+}$, $Cu(H_2NCH_2COO)^+$ and $Cu(H_2NCH_2COO)_2$, while the principal Cu(I) species is $Cu(H2NCH2COO)^{2-}$. These are referred to as $CuHL^{2+}$, CuL^+, CuL_2 and CuL^{2-}, respectively, in the following discussion. Table 3 gives the Association constants of glycine and copper glycinate species at 25 ^{o}C [22], Fig. 9 shows log

$[Cu^+]$-pH for 10^{-1} mol l^{-1} total glycine concentration, Fig. 10 shows log $[Cu^{2+}]$-pH for 10^{-1} mol l^{-1} total glycine concentration and Fig. 11 and Fig. 12 shows potential-pH diagrams for 10^{-1} mol l^{-1} total glycine concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration, for 10^{-2} M total glycine concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

Copper-Water-En System

$L = H_2NCH_2CH_2NH_2$, m = 0, p = 2, n1 = 1, n 2 = 3

Ethylenediamine (1,2-diaminoethane) is a bidentate ligand when unprotonated, Ethylenediamine can take three different forms in aqueous solutions: $^+H_3NCH_2CH_2.NH_3^+$ (H_2En^{2+}, predominant below pH 6.848), $^+H_3NCH_2CH_2NH_2$ (HEn^+) and $H_2NCH_2CH_2NH_2$ (En, predominant above pH 9.928). In the neutral form, it forms soluble complexes with both copper (I) and copper (II) ions: $Cu(H_2NCH_2CH_2NH_2)^{2+}$, $Cu(H_2NCH_2CH_2NH_2)_2^{2+}$, $CuOH(H_2NCH_2CH_2NH_2)^+$, and $Cu(H_2NCH_2CH_2NH_2)^{2+}$. These species are designated $CuEn^{2+}$, $CuEn_2^{2+}$, $CuOHEn^+$ and $CuEn_2^+$, respectively. No complexes are known involving protonated forms of En; even HEn^+ would give much weaker (monodentate) complexes than En. Table 4 gives the association constants for En and copper-En species, at 25 ^{o}C [23], Fig. 13 shows log $[Cu^+]$-pH for 10^{-1} mol l^{-1} total En concentration, Fig. 14 shows log $[Cu^{2+}]$-pH for 10^{-1} mol l^{-1} total En concentration and Fig. 15 and Fig. 16 shows potential-pH diagrams for 10^{-1} mol l^{-1} total En concentration and 10^{-2} M total dissolved Cu concentration, for 10^{-2} mol l^{-1} total En concentration and 10^{-6} M total dissolved Cu concentration.

Copper-Water-EDTA System

$L^{4-} = Y^{4-}$, m = -4, p = 6, n1 = 0, n2 = 4

Ethylenediaminetetraacetic acid can interact with up to six coordination locations of copper and similar ligands through its two-amine nitrogens and four carboxylate groups. Table 5 gives the association constants for EDTA and cupric-EDTA species at ^{o}C [23], Fig. 17 shows log $[Cu^{2+}]$-pH mol l^{-1} total EDTA concentration and Fig. 18 and Fig. 19 shows potential-pH diagrams for 10^{-1} mol l^{-1} total EDTA concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration, for 10^{-2} mol l^{-1} total EDTA concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.
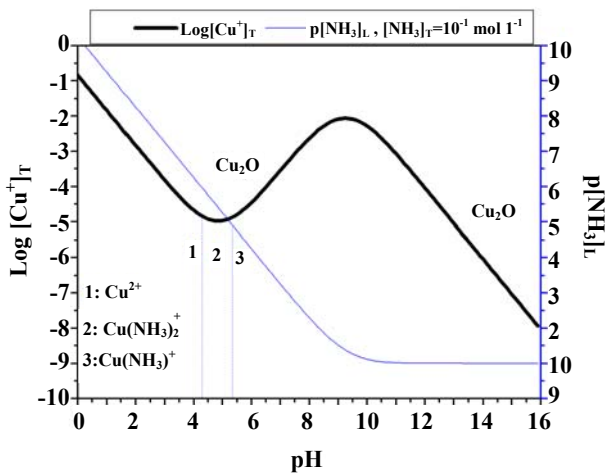
Fig. 1: *Log [Cu⁺] - pH for 10^{-1} mol l^{-1} total ammonia concentration.*
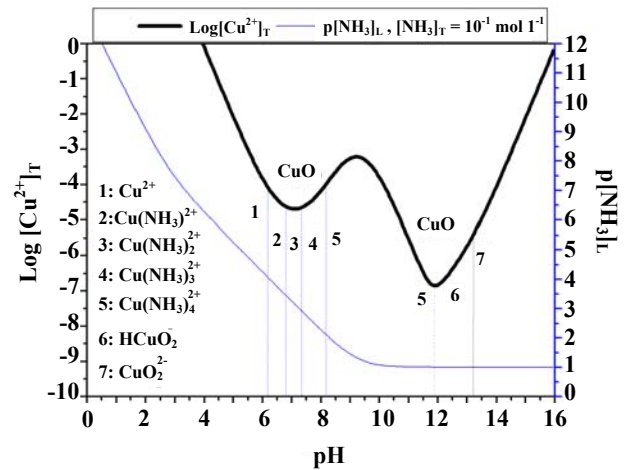
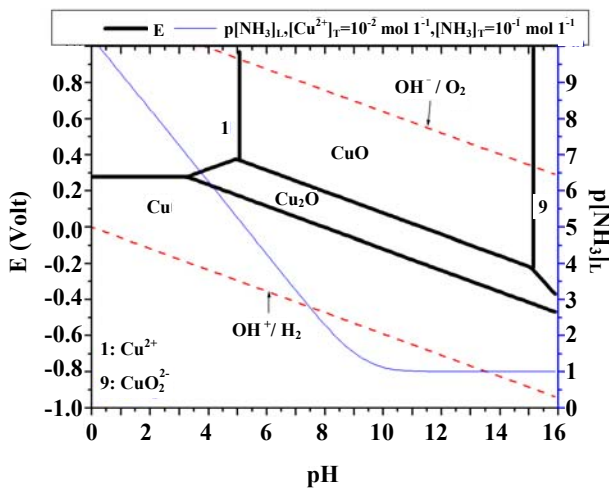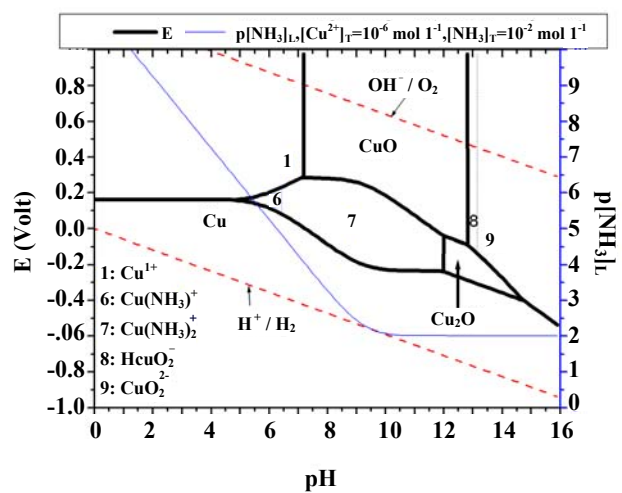**Fig. 2:** *Log [Cu²⁺] - pH for 10^{-1} mol l^{-1} total ammonia concentration.*

Fig. 3: Potential-pH diagrams for the copper-water- ammonia system at 25 ^{o}C and 1 atm 10^{-1} mol l^{-1} total ammonia concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration.

Fig. 4: Potential-pH diagrams for the copper-water- ammonia system at 25 ^{o}C and 1 atm 10^{-2} mol l^{-1} total ammonia concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

SUMMARY

Diagrams Log[Cu]-pH and Eh-pH of our method is the use diagram solubility - total concentration of ligand instead of the classical diagram solubility free concentration of ligand, the total concentration of ligand is well determined (thanks to a method numerical and data processing). Based on mass balance for metal and igands, and a combination between the two, calculation have been made with samples, in copper-water-ammonia, copper- water- cyanide, copper- water- glycine, copper-water-ethylenediamine (En) and copper-water-ethylenediaminetetraacetic acid (EDTA) systems to express equilibrium relations between solid phases and associated aqueous phase. Our rigorous calculation method permits to find the optimal conditions of dissolution (E, pH, [L]$_T$), and we realized the Eh-pH diagrams by high speed at different given conditions.

We point out that the traditional methods give an opposite result; the diagrams of distribution of species (E, pH, pL) and their data-processing exploitation become a powerful tool to contribute has to solve a serious problem of environment

This calculation method can readily be applied to other metal-ligands-water systems.

Table 1: Association constants of ammonia and copper-ammonia species, at 25 ^{o}C (I is the ionic strength [20]).

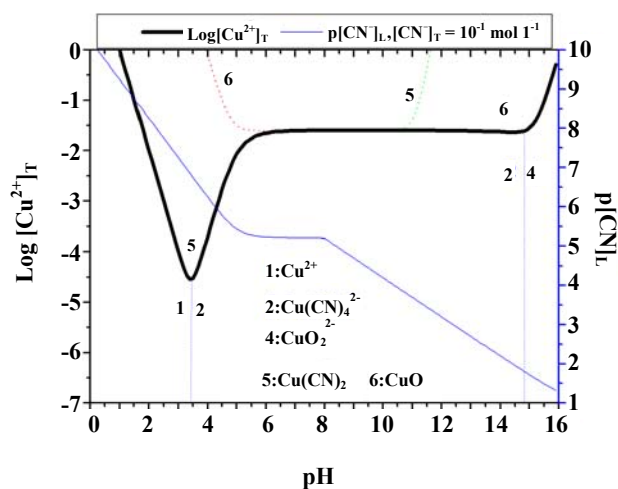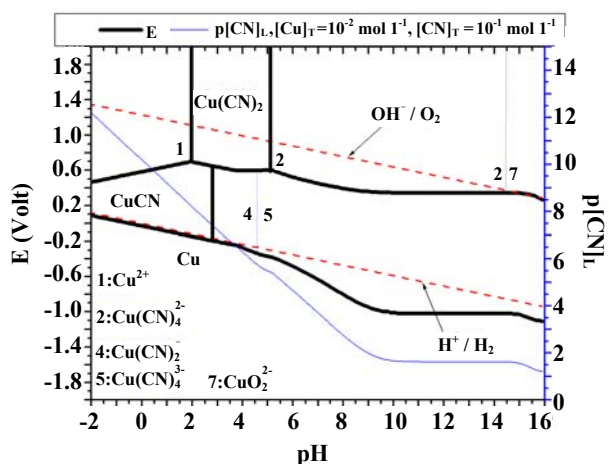| Reaction	Stability constant at 25°C and 1atm	
	Label	Log K or Log β
$L + H^+ = HL^+$	K_{LH}	9.25 (I=0)
$Cu^{2+} + L = CuL^{2+}$	K_{ML1}	4.13 (I=0.1)
$Cu^{2+} + 2L = CuL_2^{2+}$	K_{ML2}	7.61 (I=0.1)
$Cu^{2+} + 3L = CuL_3^{2+}$	K_{ML3}	10.48 (I=0.1)
$Cu^{2+} + 4L = CuL_4^{2+}$	K_{ML4}	12.59 (I=0.1)
$Cu^+ + L = CuL^+$	$β_{ML1}$	5.9 (I=2)
$Cu^+ + 2L = CuL_2^+$	$β_{ML2}$	10.8 (I=2)
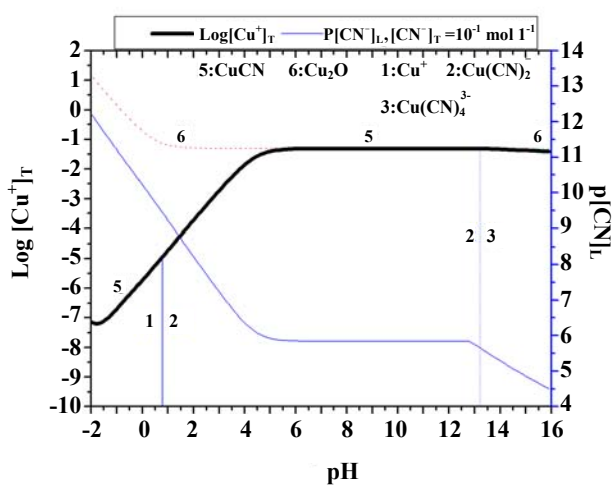
Fig. 5: Log [Cu$^+$]-pH for 10^{-1} mol l^{-1} total cyanide concentration.

Fig. 6: Log [Cu^{2+}]-pH for 10^{-1} mol l^{-1} total cyanide concentration.

Fig. 7: Potential-pH diagrams for the copper-water- cyanide system at 25 ^{o}C and 1 atm 10^{-1} mol l^{-1} total cyanide concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration.
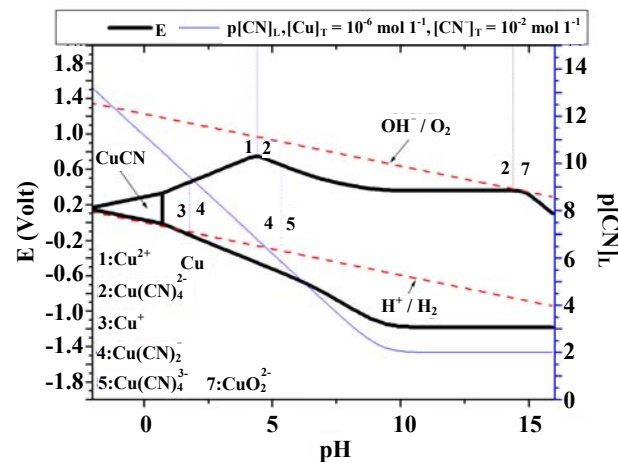
Fig. 8: Potential-pH diagrams for the copper-water- cyanide system at 25 ^{o}C and 1 atm 10^{-2} mol l^{-1} total cyanide concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

Table 2: Association constants of cyanide and copper-cyanide species at 25 ^{o}C (I is the ionic strength [18, 21]).

Reaction	Stability constant at 25°C and 1atm.	
	Label	Log K or Log β
$L^- + H^+ = HL$	K_{LH}	9.2 (I=0)
$Cu^{2+} + 4L^- = CuL_4^{2-}$	K_{ML4}	27.3 (I=0)
$Cu^+ + 2L^- = CuL^-$	$β_{ML2}$	24 (I=0)
$Cu^{2+} + 3L = CuL_3^{2+}$	$β_{ML3}$	28.6 (I=0)
$Cu^+ + 4L^- = CuL_4^{3-}$	$β_{ML4}$	30.3

Table 3: Association constants of glycine and copper glycinate species at 25 ^{o}C (I is the ionic strength [22]).

Reaction	Stability constant at 25°C and 1atm.	
	Label	Log K or Log β
$L^- + H^+ = HL$	K_{LH1}	9.778 (I=0)
$HL + H^+ = H_2L^+$	K_{LH2}	2.350 (I=0)
$Cu^{2+} + HL = CuHL^{2+}$	K_{MHL}	2.92 (I=0.1)
$Cu^{2+} + L^- = CuL^+$	K_{ML1}	8.57 (I=0)
$Cu^{2+} + 2L^- = CuL_2$	K_{ML2}	15.64 (I=0)
$Cu^+ + 2L^- = CuL_2^-$	$β_{ML2}$	10.1 (I=0.2)

Table 4: Association constants of En and copper-En species at 25 ^{o}C (I is the ionic Strength [23]).

Reaction	Stability constant at 25°C and 1atm.	
	Label	Log K or Log β
$L + H^+ = HL^+$	K_{L1}	9.928 (I=0)
$HL^+ + H^+ = H_2L^{2+}$	K_{L2}	6.848 (I=0)
$Cu^{2+} + L = CuL^{2+}$	K_{ML1}	10.48 (I=0)
$Cu^{2+} + 2L = CuL_2^{2+}$	K_{ML2}	19.6 (I=0)
$CuL^{2+} + OH^- = CuOHL^+$	K_{ML2OH}	0.73 (I=0.5)
$Cu^+ + 2L = CuL_2^+$	$β_{ML2}$	11.2 (I=0.3)
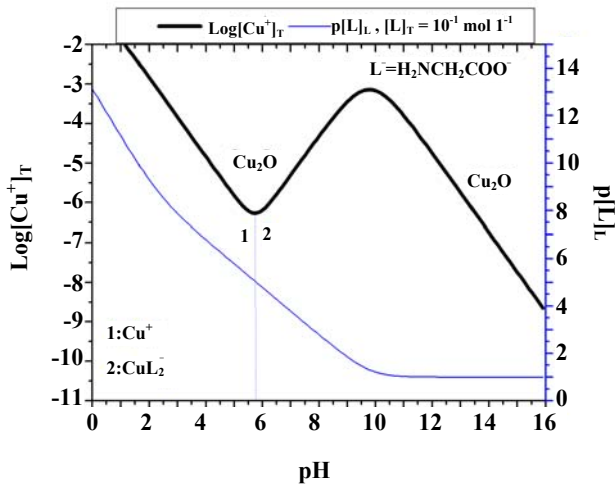
Fig. 9: *Log [Cu$^+$]-pH for 10^{-1} mol l^{-1} total glycine concentration.*
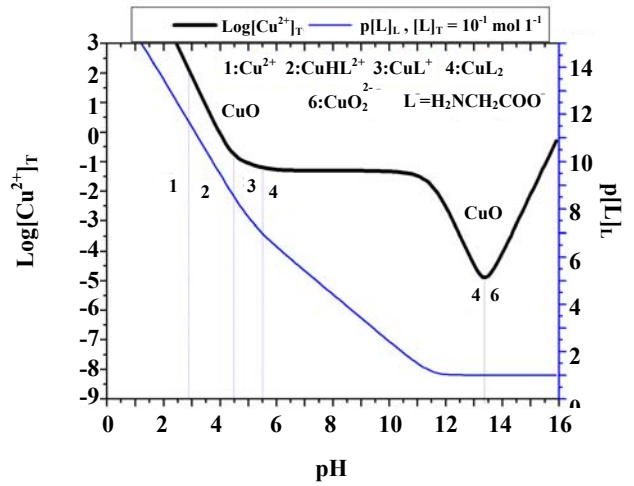
Fig. 10: *Log [Cu$^+$]-pH for 10^{-1} mol l^{-1} total glycine concentration.*
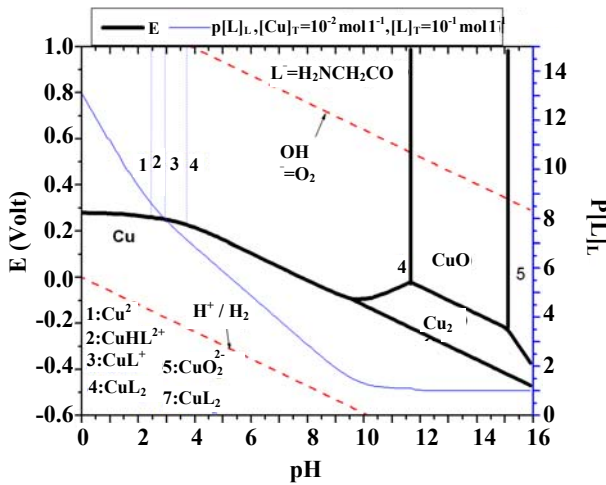

Fig. 11: *Potential-pH diagrams for the copper-water- glycine system at 25 ^{o}C and 1 atm. 10^{-1} mol l^{-1} total glycine concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration.*
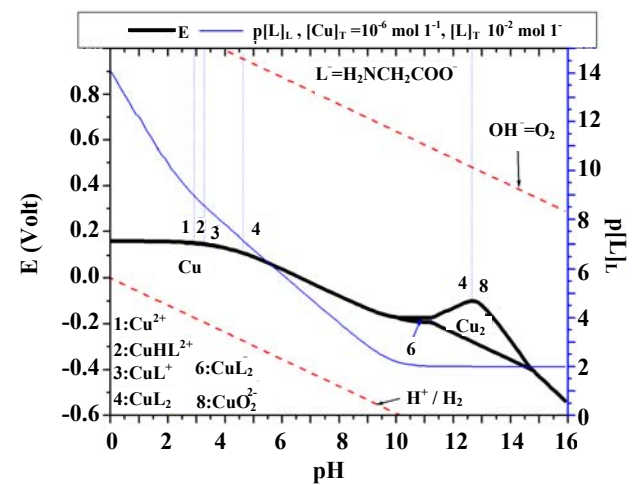
Fig. 12: *Potential-pH diagrams for the copper-water- glycine system at 25 ^{o}C and 1 atm. 10^{-2} mol l^{-1} total glycine concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.*
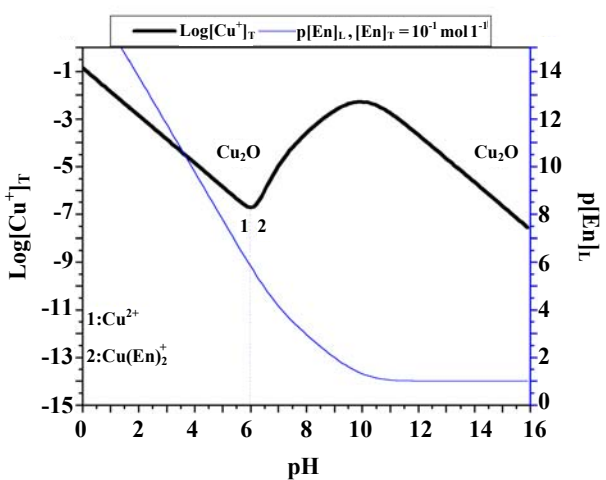
Fig. 13: *Log [Cu$^+$]-pH for 10^{-1} mol l^{-1} total ethylenediamine (En) concentration.*
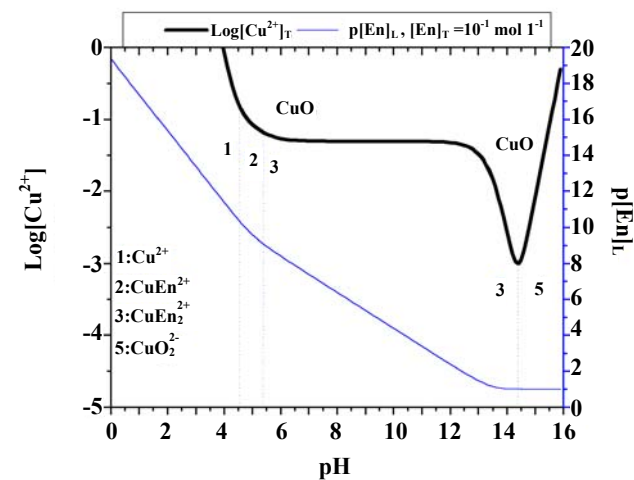
Fig. 14: *Log [Cu^{2+}]-pH for 10^{-1} mol l^{-1} total ethylenediamine concentration concentration.*

Table 5: Association constants of EDTA and copper-EDTA species at 25 °C (I=0 is the ionic strength[23]).

Reaction	Stability constant at 25°C and 1atm.	
	Label	Log K or Log β
$L^{4-} + H^+ = HL^{3-}$	K_{YH1}	11.014 (I=0)
$L^{4-} + 2H^+ = H_2L^{3-}$	K_{YH2}	17.334 (I=0)
$L^{4-} + 3H^+ = H_3L^{3-}$	K_{YH3}	20.024 (I=0.1)
$L^{4-} + 4H^+ = H_4L^{3-}$	K_{YH4}	22.024 (I=0.1)
$L^{4-} + 5H^+ = H_5L^{3-}$	K_{YH5}	23.154 (I=0.1)
$Cu^{2+} + L^{4-} = CuL^{2-}$	K_{MY1}	18.78 (I=0.1)
$CuL^{2-} + H^+ = CuHL^-$	K_{MY1H1}	3.1 (I=3.1)
$CuL^{2-} + 2H^+ = CuH_2L$	K_{MY1H2}	5.1 (I=0.1)
$CuOHL^{3-} + H^+ = CuL^{2-} + H_2O$	K_{MY1H2O}	11.4 (I=0.1)
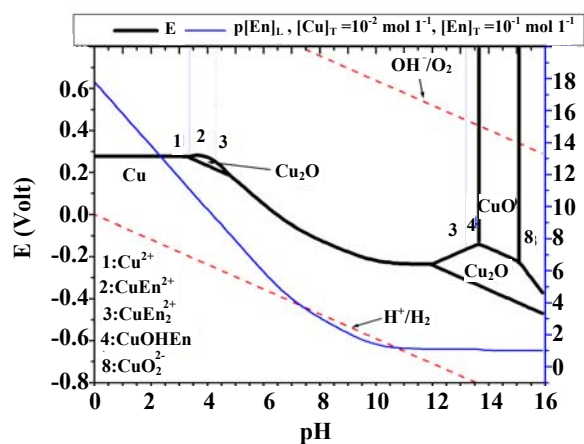
Fig. 15: Potential-pH diagrams for the copper-water- En system at 25 °C and 1 atm. 10^{-1} mol l^{-1} total ethylenediamine(En) concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration.
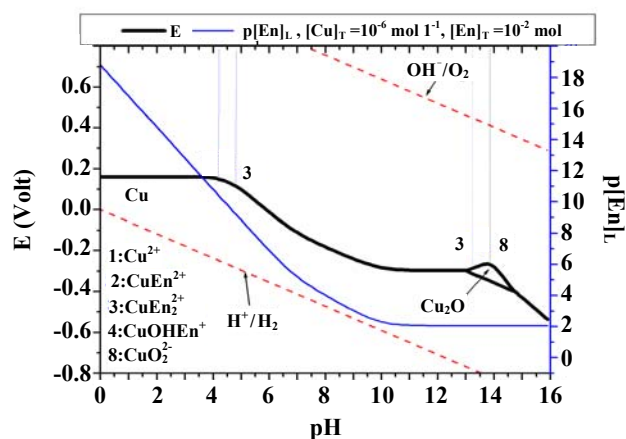
Fig. 16: Potential-pH diagrams for the copper-water- En system at 25 °C and 1 atm. 10^{-2} mol l^{-1} total En concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.
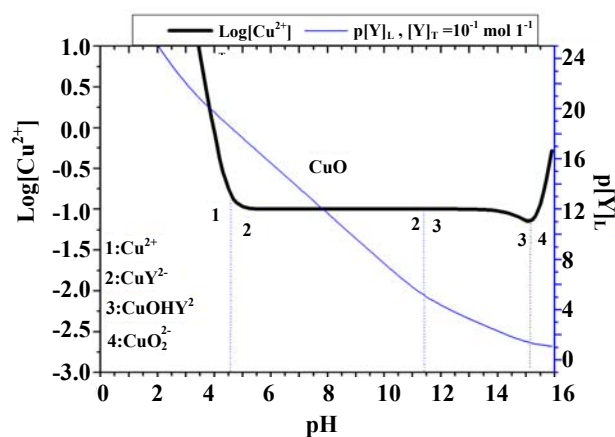
Fig. 17: Log [Cu^{2+}]-pH for 10^{-1} mol l^{-1} total EDTA concentration
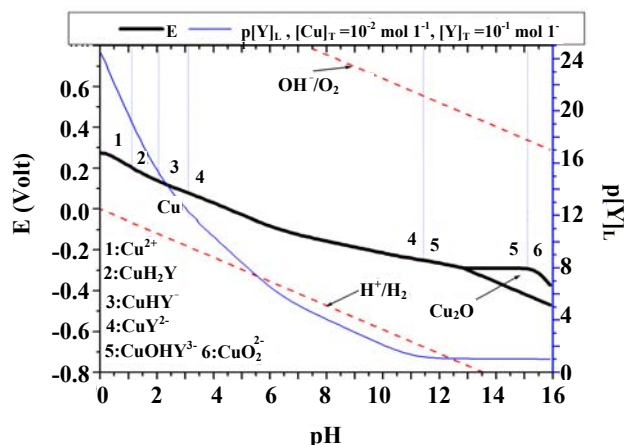
Fig. 18 : Potential-pH diagrams for the copper-water- EDTA system at 25 °C and 1 atm. 10^{-1} mol^{-1} l^{-1} total EDTA concentration and 10^{-2} mol l^{-1} total dissolved Cu concentration.
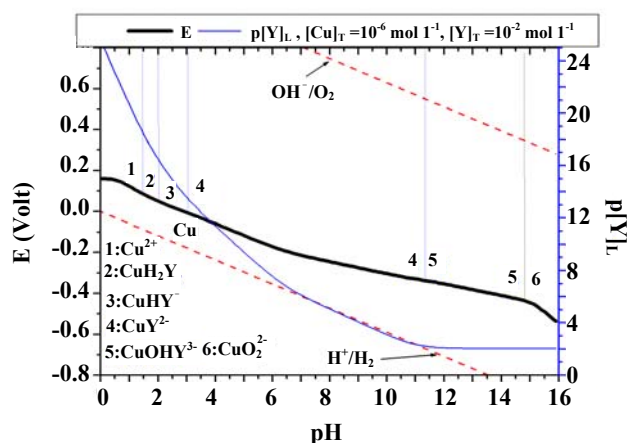
Fig. 19 : Potential-pH diagrams for the copper-water- EDTA system at 25 ^{o}C and 1 atm. 10^{-2} mol l^{-1} total EDTA concentration and 10^{-6} mol l^{-1} total dissolved Cu concentration.

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