COMPLEXATION STUDY OF HEAVY METAL ION Cu(II) WITH AMINO ACIDS BEFORE ELIMINATION BY ULTRAFILTRATION

H. Rayah^{1,✉}, B. Absar², M. R. Ghezzar¹ and F. Abed¹

¹Laboratoire des Sciences et Techniques de l'Environnement et de la Valorisation, Faculty of Sciences and Technology, University of Abdelhamid Ibn Badis- Mostaganem, BP 188, Mostaganem, Algeria

²Faculty of Computer Science and Exact Sciences, University of Mostaganem, Chemin des crêtes, Mostaganem 27000, Algeria

✉Corresponding Author: houarirayah@gmail.com

ABSTRACT

Nowadays one of the most critical issues for human life is the protection of the drinking water from contamination by heavy metals. They are toxic pollutants, which can be very dangerous for human health and the environment when they are present at high concentrations. The removal of these heavy metal ions from water has become a more than necessary issue. Ultrafiltration is considered a suitable molecular filter for the separation of big molecules, but it is still inefficient for the separation of free ions due to their weak sizes. Consequently, other methods including complexation reactions with organic ligands to trap the ions and to retain them by the membrane are considered. This work deals with the removal of toxic metallic ions by a combined complexation and -ultrafiltration process using Copper (II) ions and, amino acids as complexing agents. The complexation has been exhaustively studied by UV/visible absorbance spectrophotometry and Conductometric. The thermodynamic parameters (ΔH° , ΔG° and ΔS°) were derived and discussed for a complete description of the systems in solution and to demonstrate the importance of amino acids for trapping the metal cations by complexation processes.

Keywords: Amino Acids, Copper (II), Complexation, Ultrafiltration, UV-Visible Spectrophotometry, Conductometric, Thermodynamics.

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INTRODUCTION

Much industrial wastewaters produced by metal finishing chemicals, automotive industry, battery, aerospace, plating chemistry, mining, and general chemical processes industries, often contain heavy metals.¹ Traditional method for the elimination of these heavy metals is adsorption, ion exchange, chemical precipitation, membrane filtration, evaporation, liquid-liquid extraction, electrodeposition, crystallization, and electrochemical treatment.² However, membrane methods and ultrafiltration (UF) in particular have been described as one of the most innovative techniques in recent years in the treatment of wastewater laden with heavy metals. These membrane separation processes reflect efficiency and economic benefits with the most developed high selectivity.³

Complexation-ultrafiltration is also a promising new technique for the removal of heavy metals toxic from liquid effluents. The use of the complexing agent in combination with UF is obligatory for the elimination of heavy metals.⁴ In this work, we will present, through typical examples, the role of amino acids in the environmental and biological processes, as well as the development of therapeutic chelating in case of poisoning by toxic metals.⁵⁻⁹

Various techniques are used to determine free metal ion concentrations in the solution. In this work, we are particularly interested in the complexation of Copper (II) with ten different amino acids. The present study will be divided into two parts: The first one concern-an experimental spectroscopy investigation on the patterns of the amino acid compared to Copper (II) in the water at a temperature of 298 K. The spectroscopic physical quantities were established using the Benesi-Hildebrand equation, such as the association constant (K^{AD}) and the molar extinction coefficients (ϵ^{AD}) of each complex. Moreover,

the energy absorption (E^{CT}), and the ionization potentials of the complexes (I^p), were determined.¹⁰⁻¹⁶

The second part of the work deals with the study of the behavior of the various complexes by conductometry at infinite dilution in water. The molar conductivity (Λ) and molar conductivity at infinite dilution (Λ_0) for the ten complexes in water was measured at a temperature of 298 K. The thermodynamic quantities including the standard Gibbs free energy (ΔG°), the Enthalpy (ΔH°) and the Entropy (ΔS°) for the process of the ion association were calculated.

EXPERIMENTAL

Instrumentation

The UV absorption spectra were recorded on a PerkinElmer Lambda (25 UV-VIS) spectrophotometer in a quartz cuvette (1.0 cm path length). Conductivity readings were taken with a Suntex, model SC- 170 conductivity meter.

Chemicals

All chemicals used were prepared using analytical grade chemicals and double-distilled water. Sarcosine (Sar, 98%), threonine (The, 99.5%), serine (Ser, 99%), glutamate (Glu, 99%), aspartate (Asp, 98%), arginine (Arg, 99.5%), methionine (Met, 99%), Cysteine (Cys, 99%), tryptophane (Try, 99%) and phenylalanine (Phe, 99%) were purchased from Fluka (Fig.-1), while copper nitrate hemi pentahydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}]$ was purchased from Merck.

Fig.-1: Structures of Chemical Donors

Preparation of standard solutions of the donors and acceptor

All the solutions were based on 100 cm³ of water for the spectrophotometric measurements. Measurements of electronic spectra have been carried out in an aqueous solution of variable donor and acceptor at concentrations of 10⁻² and 10⁻⁴ mole.l⁻¹ between 190 and 1100 nm. The wavelength maxima were characterized at a temperature of 298 K.

For conductometric measurements, stock solutions of copper and different amino acids are initially prepared at concentrations of 10⁻¹ mol.l⁻¹ of the donor and the acceptor. For each step and each complex, 50 ml of the desired solution is placed in a beaker that is adjusted to the corresponding value of the

conductivity simultaneously the absorbance (*ABS*) is measured. Then, the solution was half diluted. Again, 50 ml of the taken solution conductivity and absorbance (*ABS*) is measured. The operation is repeated until the conductivity of the solution reaches that of water (pH = 7 and the specific conductance of water was less than 2 - 4,5 $\mu\text{S} \cdot \text{cm}^{-1}$).

The proposed structure of metal complexation between heavy metal ion Cu (II) and Amino acid is presented in Fig.-2.

Fig.-2: Proposed Structure of the Complex

RESULTS AND DISCUSSION

Spectroscopic Study

The (K^{AD}), and (ϵ^{AD}) of each complex, were determined from UV-Vis spectra using both modified and non-modified Benesi-Hildebrand (Eq. (1) and Eq. (2)).

$$[A_0]/ABS = 1/(K^{AD} \epsilon^{AD} [D_0]) + (1/\epsilon^{AD}) \quad (1)$$

$$[A_0]/A^a = 1/(K^{AD} \epsilon^a [D_0]) + (1/\epsilon^a) \quad (2)$$

Where $[A_0]$ is the initial concentration of the acceptor and $[D_0]$ is the initial concentration of the donor. The following Equations used to calculate A^a and ϵ^a are mentioned in more details in the reference work by Benesi-Hildebrand.¹⁷

The ionization potential was calculated by using two methods by equations (3) and (4):¹⁴⁻²¹

$$h\nu_{CT} = I^D - C_1 + [C_2/(I^D - C_1)] \quad (3)$$

$$h\nu_{CT} = aI^D + b \quad (4)$$

$$I^D = 4,39 + 0,857 h\nu_{CT} \quad (5)$$

$$I^D = 5,1 + 0,7 h\nu_{CT} \quad (6)$$

$h\nu_{CT}$: Absorption band energy of CT complex, and h : Planck's constant, $C_1 = 5.2$ eV, $C_2 = 1.5$ eV², $a = 0.87$ or 0.67 , $b = -3.6$ or -1.9 .

Where $h\nu_{CT}$ is the absorption band energy of the charge transfer complex in eV., I^D is the ionization potential of the donor in eV. C_1 , C_2 , a , and b in Equations 5 and 6 are constants.

From complexes, D₁ to D₁₀ new absorption bands are shown in the visible region whose wavelengths are 760, 710, 760, 740, 760, 665, 750, 750, 710, and 760 nm, respectively. Whereas, the appearance of a band at 810 nm associated with the acceptor is reported (Table-1).

The values of K^{AD} and ϵ^{AD} are determined by plotting a graph (Eq.-7):

$$[A_0]/A = f(1/[D_0]) \quad (7)$$

Table-1: Charge-transfer Absorption Maxima of Cu (II) with Different Donors

Donors	λ_{max} (nm) Complex	$(\Delta\lambda / \lambda) \cdot 10^{+5}$
Sarcosine (D ₁)	760	1,316
Threonine (D ₂)	710	1,408
Serine (D ₃)	760	1,316
Glutamate (D ₄)	740	1,351
Asparatate (D ₅)	760	1,316
Arginine (D ₆)	665	1,504
Methionine (D ₇)	750	1,333
Cysteine (D ₈)	750	1,333
Tryptophane (D ₉)	710	1,408
Phenylalanine (D ₁₀)	760	1,316

In general, the variation of $[A_0] / A^a$ against $1 / [D_0]$ leads to a linear relationship. A rough estimation of ϵ^{AD} and K^{AD} of the complexes can be calculated and used for the nonlinear relationship.²² The estimated values of K^{AD} and ϵ^{AD} were obtained from the plots.²³ The values of K^{AD} and ϵ^{AD} for all complexes are shown in Table-2. The corresponding plots are displayed in Fig.-3, with good correlation factors ($R^2 > 0,98$).

Fig.-3: Benesi-Hildebrand Plots of the Complexes D₃ and D₆ at 298 K

Molar absorptivity's, ϵ^{AD} , obtained from Eqn.-1, are 18.886, 18.765, 18.997, 16.666, 19.948, 81.967, 20.738, 19.782, 18.663, and 19.892. $\text{l.cm}^{-1} \text{mol}^{-1}$ for complexes D₁ to D₁₀, while the values of K^{AD} , are given in Table-2. These 2834, 1672, 1424, 2566, 122, 1380, 1650, 1020 and 1274 ($\text{dm}^3 \cdot \text{mole}^{-1}$) allow the establishment of the stability order for identical complexes as follows:

$[\text{D}_1/\text{Cu (II)}] > [\text{D}_5/\text{Cu (II)}] > [\text{D}_2/\text{Cu (II)}] > [\text{D}_8/\text{Cu (II)}] > [\text{D}_3/\text{Cu (II)}] > [\text{D}_4/\text{Cu (II)}] > [\text{D}_7/\text{Cu (II)}] > [\text{D}_{10}/\text{Cu (II)}] > [\text{D}_9/\text{Cu (II)}] > [\text{D}_6/\text{Cu (II)}]$

Table-2: Association Constants and Molar Extinction Coefficient for each Complex.

Donors	K^{AD} (l.mol^{-1})	ϵ^{AD} ($\text{l.cm}^{-1} \cdot \text{mole}^{-1}$)
Sarcosine (D ₁)	2834	18.886
Threonine (D ₂)	1672	18.765
Serine (D ₃)	1590	18.997
Glutamate (D ₄)	1424	16.666
Asparatate (D ₅)	2566	19.948
Arginine (D ₆)	122	81.967
Methionine (D ₇)	1380	20.738
Cysteine (D ₈)	1650	19.782
Tryptophane (D ₉)	1020	18.663
Phenylalanine (D ₁₀)	1274	19.892

The greater stability of the complex $[D_1/Cu(II)]$ could be explained by the presence of the inductive effect of the methyl group donor. The same explanation can be given for the highest stability of the complex $[D_2/Cu(II)]$ compared to the complex $[D_3/Cu(II)]$. Unlike the complex $[D_6/Cu(II)]$, the inductive effect of withdrawing nitrogen atoms appears significantly diminishes the stability of the complex. As complex $[D_7/Cu(II)]$ and $[D_8/Cu(II)]$, the latter is less stable because of the important attracting inductive effect of CH_3-S group compared to the group $H-S$. Regarding the complexes $[D_4/Cu(II)]$ and $[D_5/Cu(II)]$, the distance coordination sites $[D_4/Cu(II)]$ by its analog seem significantly decrease the stability of the complex. Furthermore, when comparing the stability of the complexes of aromatic amino acids, it is influenced not only by the electronic character of the methyl substituents but also by their steric effects: the complex $[D_{10}/Cu(II)]$ appears more stable than the complex $[D_9/Cu(II)]$ because of the flatness of the former.

The stability of the complexes of aliphatic amino acid compounds is greater than that of the aromatic amino acids due to the solvation of polar solvents (aqueous); water molecules prevent the copper ions approach the nucleus aromatic. It may be noted that the more complex charge transfer bandwidth, the higher the stability of the complex is great, and the electronic transfer phenomenon of the donor to the acceptor is complete. $[D_6/Cu(II)]$ seems to be most sensitive to light in the visible. The presence of nitrogen atoms in this complex could be the cause of this sensitivity.

The absorption band energy, E_{CT} , was calculated by using Eq.-8:

$$E_{CT} = h \nu_{\max} = hc / \lambda_{\max} \quad (8)$$

Where C is the speed of light in a vacuum, $\lambda_{\max}$ is the wavelength, and h is the Planck constant.

The absorption band wavelengths and energy absorption band for each complex are shown in Table-3.

Table-3: Absorption Band Wavelengths, Energy Absorption Band for each Complex.

Donors	$\lambda_{\max}$ (nm)	E_{CT} (eV)	$(\Delta E_{CT} / E_{CT}).10^{+5}$
Sarcosine (D_1)	760	1,631	1,316
Threonine (D_2)	710	1,746	1,408
Serine (D_3)	760	1,631	1,316
Glutamate (D_4)	740	1,675	1,351
Aspartate (D_5)	760	1,631	1,316
Arginine (D_6)	665	1,864	1,504
Methionine (D_7)	750	1,653	1,333
Cysteine (D_8)	750	1,653	1,333
Tryptophane (D_9)	710	1,746	1,408
Phenylalanine (D_{10})	760	1,631	1,316

The ionization Potential I^D of the different amino acids, complexing Copper (II) determined by the eqns.-3 to 6 when the variation of mean values of I^D is ranging from 7,637 to 8,265 eV, as shown in Table-4.^{24,25}

Table-4: Ionization Potentials I^D of the Various Amino Acid

Donors	I^D (eV)				
	Eqn.-3	Eqn.-4	Eqn.-5	Eqn.-6	Average Value
Sarcosine (D_1)	7,976	7,915	7,342	7,511	7,686
Threonine (D_2)	8,805	8,539	7,818	7,900	8,265
Serine (D_3)	7,976	7,915	7,342	7,511	7,686
Glutamate (D_4)	8,278	8,142	7,515	7,653	7,897
Aspartate (D_5)	7,976	7,915	7,342	7,511	7,686
Arginine (D_6)	7,906	7,862	7,301	7,478	7,637
Methionine(D_7)	8,123	8,025	7,426	7,580	7,788
Cysteine (D_8)	8,123	8,025	7,426	7,580	7,788
Tryptophane (D_9)	8,805	8,539	7,818	7,900	8,265
Phenylalanine (D_{10})	7,976	7,915	7,342	7,511	7,686

Conductometric Study

The molar conductance (Λ) for all studied complexes was evaluated by the following relation (Eq.-9):

$$\Lambda = 1000 \sigma / C \quad (9)$$

Where (σ) is the measured specific conductance in ($\mu\text{S}/\text{cm}$), and C the molar concentration of the solution. The equivalent conductance (Λ) for all studied systems was recorded in Table-5.

The use of the Kohlrausch equation showed experimentally that the equivalent conductivity for each concentration of amino acid at a given temperature was plotted against the square root of concentration $C^{1/2}$ as shown in Fig.-4. The limiting value of the molar conductivity $\Lambda_0 = \Lambda (C \rightarrow 0 \text{ mol/l})$ was obtained by linear extrapolation of the $\Lambda (C^{1/2})$.^{26,27}

Fig.-4: Equivalent Conductance (Λ) as a Function of $C^{1/2}$ of the Complexes D₂ and D₁₀ at 298 K

Arrhenius suggested that the degree of dissociation or ionization has can be calculated by the report Eq.-10:

$$\alpha = \Lambda / \Lambda_0 \quad (10)$$

The absorbance of each complex is measured to the maximal wavelength characterizing (λ_{max}) it. From the degree of dissociation, α , of weak electrolyte, one can calculate the constant of dissociation, K_a , of this electrolyte by the report Eq.-11:

$$K_a = (\alpha^2 \cdot C) / (1 - \alpha) \quad (11)$$

The thermodynamic quantities as calculated, from the Benesi-Hildebrand plot, are shown in Table-5. Knowing the values of K_a , the values of standard Gibbs energy ΔG^0 , entropy ΔS^0 , and enthalpy ΔH^0 for each [Amino acid / Cu (II)] interaction were evaluated using the following thermodynamics eqns.-12 and 13.

$$\Delta G^0 = -RT \ln K^{AD} \quad (12)$$

$$\Delta H^0 = \Delta G^0 + T \Delta S^0 \quad (13)$$

R is the ideal gas constant.

The enthalpy ΔH^0 was illustrated by the Vant-Hoff equation (Eq.-14) in the temperature range from (298–314 K).²⁸

$$\ln K^{AD} = -(\Delta H^0 / RT) + c \quad (14)$$

As shown in Table-5 the enthalpy of association (ΔH^0) of the complexes negative which means that the formation of the metal complexes occurs via exothermic hydration.²⁹

Moreover, a variation of ΔG^0 values is noted from the D₁ to D₁₀ complexes formation reactions corresponding to K^{AD} such, -12,038, -17,354, -17,912, -18,112, -18,191, -18,467, -18,560, -18,593, -19,666 and -19,915 KJ. mole⁻¹. The negative value of standard Gibbs energy ΔG^0 for the complexes suggests a spontaneous nature of such processes.³⁰ The spontaneity of these reactions follows the trend: [D₆/Cu(II)] > [D₉/Cu(II)] > [D₁₀/Cu(II)] > [D₇/Cu(II)] > [D₄/Cu(II)] > [D₃/Cu(II)] > [D₈/Cu(II)] > [D₂/Cu(II)] > [D₅/Cu(II)] > [D₁/Cu(II)]

The values of entropy ΔS^0 were also negative due to the negative values of enthalpy ΔH^0 . This is due to contributions from both the formation of ion pairs and the ordering of the system because of association under the influence of solvation and columbic effect in spontaneous continuum media.

Table-5: Conductance and Thermodynamics Parameters for the Complexes

Λ (S.Cm ² .mol ⁻¹)										
C (mol / l)	[D ₁ /Cu]	[D ₂ /Cu]	[D ₃ /Cu]	[D ₄ /Cu]	[D ₅ /Cu]	[D ₆ /Cu]	[D ₇ /Cu]	[D ₈ /Cu]	[D ₉ /Cu]	[D ₁₀ /Cu]
0,10000	194,192	250,437	224,006	207,062	194,192	263,009	94,2000	174,054	207,142	243,566
0,05000	230,974	305,801	254,801	216,171	230,974	283,159	113,200	203,445	251,434	301,921
0,02500	259,884	351,971	288,960	268,187	259,884	296,362	129,720	227,645	279,899	331,147
0,01250	302,186	409,077	339,571	301,284	302,186	311,475	140,080	272,199	311,304	352,727
0,00625	316,679	481,188	382,790	361,493	316,679	383,222	152,160	312,256	325,126	378,887
0,00312	314,752	519,782	402,059	409,217	314,752	407,424	160,960	311,06	336,173	407,725
0,00156	404,611	584,502	453,005	456,087	404,611	451,843	167,104	350,123	356,609	425,415
0,00078	454,882	604,984	537,298	625,392	454,882	754,096	180,864	367,806	380,667	472,084
Λ_0 (S.Cm ² /mol)	645,085	800,215	599,338	638,751	650,046	799,244	225,245	550,125	501,245	520,123
K _a (l/mol)	2834	1672	1590	1424	2568	122	1380	1650	1020	1274
ΔG^0 (KJ/mol)	-18,593	-18,467	-18,467	-18,191	-19,666	-12,038	-18,112	-18,561	-17,354	-17,912
ΔH^0 (KJ/mol)	-38,451	-38,451	-37,758	-37,102	-39,568	35,012	-36,235	-37,254	-35,758	-36,122
ΔS^0 (J/mol K)	-63,461	-63,461	-66,782	-63,460	-66,782	-87,154	-60,815	-62,731	61,758	-61,107

CONCLUSION

The spectrophotometric analysis confirmed that complexes are formed in the solution so which is endorsed by the Benesi-Hildebrand equation. The thermodynamic study allowed us to calculate the variation of the enthalpy ΔH and that of the enthalpy ΔS of the formation and rearrangement of ion pairs to elucidate the different ion-solvent interactions for our systems; The negative value of the standard Gibbs energy ΔG^0 for the complexes suggests the spontaneous nature of such processes and confirmed more stability of the complex.

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