



Formation and Association Constants of $MnCl_2$, $NiCl_2$ and $CuCl_2$ with Glycine, Lysine and Cysteine in Aqueous Solution at 293.15 K

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Authors' contributions

This work was carried out in collaboration between all authors. Author FIED designed the study, performed the experiments and different conductometric calculations, wrote the protocol and the first draft of the manuscript. Author NMH performed the Semi-empirical PM3 calculations of the studied systems. Author SET managed the literature searches and publication processes and also give final approval of the version to be submitted and any revised version. All authors read and approved the final manuscript.

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ABSTRACT

The complexation reactions between different amino acids (Glycine, L-Lysine, and L-Cysteine) and transition metal cations (Ni^{2+} , Cu^{2+} , and Mn^{2+}) were studied conductometrically in water at 293.15 K. The formation constants (K_f) of the resulting complexes were calculated from the computer fitting of the molar conductance (Λ)-mole ratio (L/M) data. Semi-empirical PM3 calculations were also used to predict the structure of the metal complex by calculating the enthalpy of formation, the geometrical parameters, refractivity, dipole moment and polarizabilities of the suggested structures of the formed complexes in the gaseous state. The association constant (K_a) of $MnCl_2$, $NiCl_2$ and $CuCl_2$ in aqueous solution in the absence and in the presence of glycine and lysine amino acids at 293.15 K were also determined conductometrically. The conductance data for the association process were analyzed using Shedlovsky conductance equation. The free energy changes of the complexation and association processes were evaluated from the temperature dependence of

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formation and association constants. A computer program was used for calculating the molar conductance, the limiting molar conductance (Λ°), the formation constant, the association constant, the free energy change of formation (ΔG_f) and association (ΔG_a) processes, Walden product ($\Lambda \cdot \eta$) and the triple-ion association constant (K_3). The results indicate the formation constant of Mn^{2+} and Cu^{2+} with glycine is more in general than that with cysteine and lysine. The results also indicate that the association constant of the studied salts increase in the presence of the amino acids under consideration (glycine and lysine) comparing to that in the absence of these amino acids. The effect of glycine on the association of the studied salts was found to be less than that of lysine. Also the formation and the association processes are spontaneous one.

Keywords: Formation constant; association constant; Walden product; amino acids.

1. INTRODUCTION

There are 20 basic amino acids found in all living organisms. These compounds have an amino group and a carboxyl group, which ionize in aqueous solutions and give rise to zwitterionic amino acid molecules in the neutral pH range. The zwitterionic amino acid molecules have a large dipole moment, which gives rise to important interactions with individual ions. From the amino acids there are two amino acids; L-Lysine and L-Cysteine. L-Cysteine, is the precursor of many industries such as the pharmaceutical, food, flavors and personal-care industries [1] and as a processing aid for baking. [2] L-Cysteine has been proposed also as a preventative or antidote for some of the negative effects of alcohol, including liver damage and hangover. [3] The formation of disulfide bonds in Cysteine play role in crosslinking proteins, resulting in an increase in the proteins rigidity and proteolysis resistance. Disulfide bridges between cysteine residues, inside the cell, support the protein's tertiary structure. An example of a protein with cysteine crosslinking is the Insulin [4]. In the body, L-Lysine is a considered as building block for all protein. Also, L-Lysine plays a major role in Ca absorption; recovering from surgery or sports injuries, building muscle protein; and the body's production of enzymes, hormones, and antibodies. [5] Cysteine as a neutral amino acids have an basic group and acidic group, resulting in zwitterionic molecules in the neutral range of pH. Basic amino acids such as lysine have two amino groups and one carboxyl group, which also give rise to zwitterionic molecules with basic amino group. Some studies have used the electrolytic conductance measurements for studying the interaction of some ligands with some metal cations and determination of the formation constants of the formed complexes. [614] The ion-pair association of different metal salts in different aqueous and organic-aqueous solutions was also reported. [15-24] Little

studies were focusing their attentions on the effect of the presence of someorganic igands on the association with metal salts indifferent solutions [25-27] The present work aims to study conductometrically the interaction between some amino acids (glycine, L-cysteine and L-lysine) with some transition metal salts ($MnCl_2$, $NiCl_2$ and $CuCl_2$) in aqueous solution at 293.15 K. Also this work aim to study conductometrically the effect of some amino acids (glycine and L-lysine) on the association behavior of the transition metal salts under consideration ($MnCl_2$, $NiCl_2$ and $CuCl_2$) in aqueous solution at 293.15 K. Also this study aim to report semi-empirical PM3 calculations to predict the structure of the metal complex formed in the gaseous state between the studied amino acids and transition metal cations.

2. EXPERIMENTAL

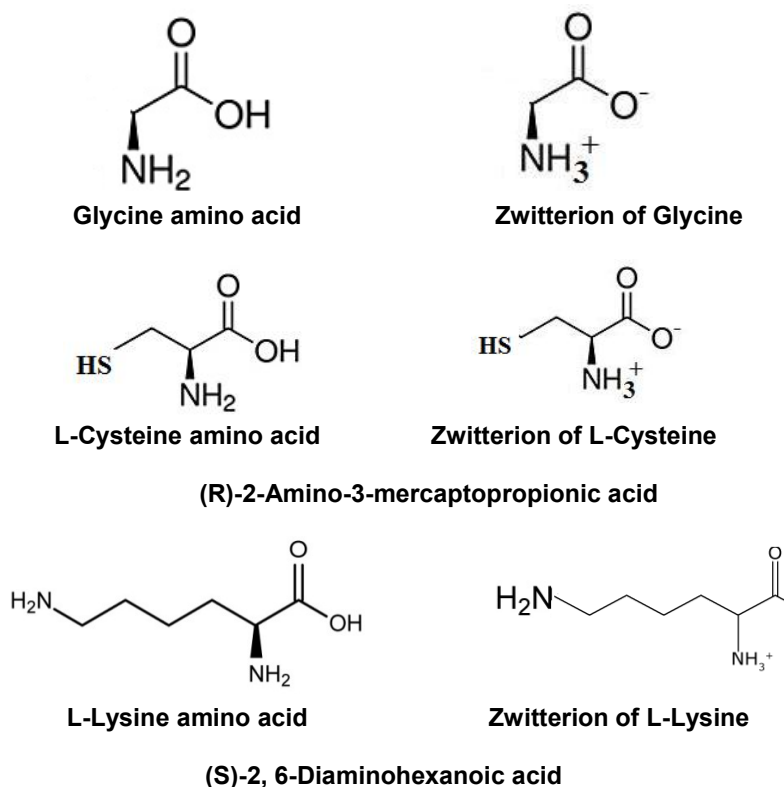
Chemicals: $MnCl_2$, $NiCl_2$ (Top Chem., Egypt, 98%), $CuCl_2$ (El-Nile Company, Egypt, 98%), Glycine (El-Nasr Company, Egypt, 99%), L-Lysine (India, 99%) and L-Cysteine (India, 99%) (Scheme 1).

Solutions: Bidistilled water was used to prepare the following aqueous solutions: Solutions of amino acids (0.01 M) and solutions of transition metal salts (0.001 M).

2.1 Apparatus and Procedures

The conductance measurements of the prepared salt solutions were carried out using Jenway Conductivity Bridge (4310) of a cell constant value 0.96 cm^{-1} and a deviation of $\pm 0.1 \mu\text{S}\cdot\text{cm}^{-1}$. The cell constant was determined with potassium chloride solutions [28].

The Conductivity Bridge was connected to MLW 3230 ultrathermostate to maintain the temperature constant at the desired temperature ($\pm 0.005^\circ\text{C}$).



(Scheme 1)

(i) For the formation constant determination; 30 ml of the desired transition metal salts (0.001M) were placed in a double jacket glass cell and the specific conductance (κ) of the solution was measured. A known amount of an amino acid solution (0.01M) was added (0.2 ml.) in a stepwise manner using a burette. After each addition the solution stirred and then the specific conductance of the solution was measured. The amino acid solution was continually added until the desired amino acid-cation mole ratio was achieved.(ii) For the association constant determination;

- a) 30 ml of bidistilled water were placed in a double jacket glass cell, and then the specific conductance was measured. A known amount of the metal salt solution (0.01 M) was added (0.2 ml.) in a stepwise manner using a micropipette. The solution stirred and then the specific conductance of the solution was measured after each addition. The metal salt solution was continually added until the desired concentration of the metal salt solution.
- b) 30 ml of the desired amino acid solution (0.001M) was placed in a small clean

beaker and the specific conductance of solution was measured. A known amount of the metal salt solution (0.01 M) was added (0.2 ml.) in a stepwise manner using micropipette. The solution stirred and then the specific conductance of the solution was measured after each addition. The metal salt solution was continually added until the desired concentration of the metal salt solution.

3. RESULTS AND DISCUSSION

3.1 Formation Constant Determination

For the determination of the formation constant of the formed complexes between the transition metal cations (Mn^{2+} , Ni^{2+} , Cu^{2+}) and the amino acids (glycine, L-cysteine and L-lysine), the specific conductance (κ) were measured as explained in the experimental section at 293.15 K in aqueous solution. The resulting specific conductance show that, the addition of the ligand to the metal salt solution causes a gradual decrease in the specific conductance, which tends to level off at high ligand to metal ion mole

ratios. The molar conductance (Λ) was calculated applying Eq. (1)

$$\Lambda = 1000 \kappa / C \quad (1)$$

Where, (C) the molar concentration of the transition metal cation solutions. The molar conductance was plotted versus [L/M] as shown in the Figs. (1-3). As in the figures, breaks were shown at different amino acid / transition metal cation ratios 1:1, 2:1 and 3:1 [L/M]. The formation constants (K_f) for metal ion-amino acid stoichiometric complexes can be expressed as in equation (2) according to Takeda et. al. [10]:

$$K_f = \frac{(\Lambda_m - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_c)[L]} \quad (2)$$

Where

$$[L] = [L]_t - \frac{[M]_t(\Lambda_m - \Lambda_{obs})}{(\Lambda_m - \Lambda_c)} \quad (3)$$

Where, Λ_m =molar conductance of metal ion before addition of the ligand (amino acid), Λ_{obs} =observed molar conductance of the solution during the titration, Λ_c =molar conductance of the complexed metal ion, $[M]_t$ =total metal salt concentration, and $[L]_t$ =total ligand concentration, and $[L]$ =free ligand concentration. The formation constants (K_f) for metal ion-amino acid complexes were presented in Table (1) and expressed in Figs (4-5). The values of the change free energy of formation (ΔG_f°) were calculated using the following equation and presented in Table (1):

$$\Delta G_f^\circ = - 2.303 RT \log K_f \quad (4)$$

Where, R is the gas constant and T is the absolute temperature.

As shown from Table 1 and Figs.(4 -5), the formation constants of the formed complexes between $MnCl_2$, $NiCl_2$ and $CuCl_2$ and glycine, cysteine and lysine in aqueous solution 293.15 K can be represented as in the following orders for [L/M] complexes:

* (Mn-Gly) > (Mn-Cys) > (Mn-Lys) for all stoichiometric complexes.

* (Ni-Lys) > (Ni-Gly) > (Ni-Cys) for 1:1 stoichiometric complexes and (Ni-Gly) > (Ni-Lys)

> (Ni-Cys) for 2:1 and 3:1 stoichiometric complexes.

* (Cu-Gly) > (Cu-Lys) > (Cu-Cys) for 1:1 and 3:1 stoichiometric complexes and (Cu-Lys) > (Cu-Cys) > (Cu-Gly) for 2:1 stoichiometric complexes.

(Mn-Gly) > (Cu-Gly) > (Ni-Gly) for 1:1 stoichiometric complexes, (Mn-Gly) > (Ni-Gly) > (Cu-Gly) for 2:1 stoichiometric complexes, and (Ni-Gly) > (Cu-Gly) > (Mn-Gly) for 3:1 stoichiometric complexes.

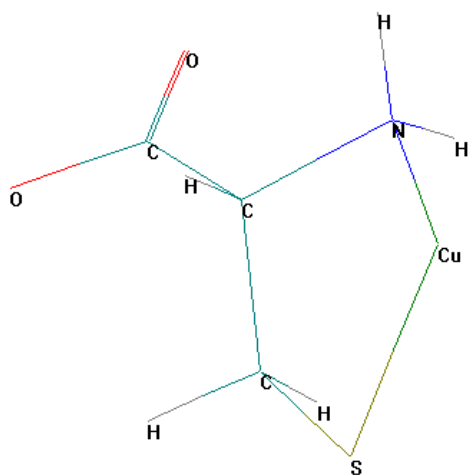
(Mn-Cys) > (Cu-Cys) > (Ni-Cys) for 1:1 and 3:1 stoichiometric complexes, and (Cu-Cys) > (Ni-Cys) > (Mn-Cys) for 2:1 stoichiometric complexes.

(Cu-lys) > (Ni-lys) > (Mn-lys) for all stoichiometric complexes. This can be explained depending on the ionic radius of the studied cations which decrease in the order: ($Mn^{+2} > Ni^{+2} > Cu^{+2}$). This order is quite in accordance with Cotton and Wilkinson.[29]

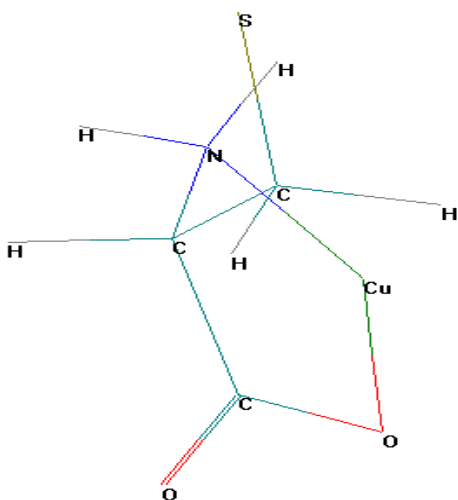
Also, it was found that the formation constants of different ratios are:

1:1 [L/M] complexes > 2:1 [L/M] complexes > 3:1 [L/M] complexes with little exceptions.

A semi-empirical PM3 calculation were also used to predict the structure of the metal complexes formed in the gaseous state between the studied amino acids and the transition metal cations under consideration. This calculations include the enthalpy of formation (ΔH), the geometrical parameters (volume, V), molar refraction (R), dipole moment (μ) and polarizabilities (α) as reported in Tables 2 and 3. As shown from the data in Table 2, the more stable complex formed in the gas state as calculated applying the semi-empirical PM3 program are that of Cu^{+2} cation with cysteine amino acid (1:1 and 2:1 L/M) through sulphur and oxygen atoms as reflected from the higher enthalpy change of formation (Scheme 2). A small increase in the enthalpy of formation, and so in the stability was found for the complexes formed through sulphur than that through oxygen atoms. This may be due to the less electronegativity of sulphur atoms than oxygen atoms and so, more donor atom and more coordinated with the metal cation than oxygen.



Cysteine- Cu⁺² (1:1 L/M) through sulphur atom



**Cysteine- Cu⁺² (1:1 L/M) through oxygen atom
(Scheme 2)**

Also as shown from **Tables 2 and 3**, it was found that the formation constants of 2:1 [L/M] are higher than that of 1:1 [L/M] amino acids-M⁺² complexes through both sulphur and oxygen atoms (Scheme 3 as example). This result is agreement with that that observed for the solid amino acids (free from sulphur atoms)-transition metal cations, that (2:1 L/M) are the stable complexes. On the other hand, this result is reverse to that noted from the conductometric experimental data of the formation constants. This anomalous behavior may be due to the competition between both of the amino acid and the solvent molecules to chelate the transition metal cation.

The same order noted from the experimental data was found from that calculated applying the semi-empirical PM3 program as follow: (Cu-lys, cys) > (Ni-lys, Cys) > (Mn-lys, Cys) for all stoichiometric complexes.

The semi-empirical PM3 calculation indicate that the stability of cysteine-M⁺² complexes are higher than that lysine- M⁺² complexes. These results are in agreement with that obtained from the experimental data onto Mn⁺² while not fully in agreement with Ni⁺² and Cu⁺².

3.2 Association Constant Determination

The specific conductance (κ) of different concentrations (C, in the range 1.96×10^{-4} to 9.09×10^{-4} M) of MnCl₂, NiCl₂ and CuCl₂ in aqueous solution in the absence and in the presence of glycine and lysine amino acids at 293.15 K were measured as explained in the experimental section and the molar conductance, Λ was calculated applying **Eq. (1)**. The limiting molar conductance, Λ° of MnCl₂, NiCl₂ and CuCl₂ in aqueous solution in the absence and in the presence of glycine and lysine amino acids at 293.15 K were determined from the intercept of the graphical relations (Figures 6-8) of Λ versus $C^{1/2}$ according to the Onsager relation [30].

The experimental data for conductance measurements were analyzed using Shedlovsky [31] extrapolation techniques, to get the association constant of the salts under consideration, which follows equation:

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda^\circ} + \frac{K_a C \Lambda S(z) \gamma_i^2}{\Lambda^\circ{}^2} \quad (5)$$

S(z) is the Shedlovsky function, which can be calculated as follow:

$$S(z) = \left\{ \frac{z}{2} + \sqrt{1 + (z/2)^2} \right\}^2, \quad z = A \frac{\sqrt{CA}}{\Lambda^\circ{}^{3/2}} \quad (6)$$

A is the Onsager coefficient = $8.2 \cdot 10^5 \Lambda^\circ / (\epsilon T)^{3/2} + (82/\eta_0) (\epsilon T)^{1/2}$ where ϵ is the relative permittivity, η_0 is the viscosity of the solvent and T is the absolute temperature. γ_i is the mean activity coefficient estimated from the Debye-Huckel limiting law as modified by Robinson and Stokes. Using the data of (Λ), S (z) and (Λ°), the values of degree of dissociation (α) were calculated by using the following equation:

$$\alpha = \Lambda S(z) / \Lambda^\circ \quad (7)$$

Using these (α) and (ϵ) values, the mean activity coefficients (γ_{\pm}) were evaluated by means of:

$$\log \gamma_{\pm} = -\frac{Z_+Z_-A\sqrt{C}}{1+B r^{\pm}\sqrt{C}} \quad (8)$$

Where, Z_- , and Z_+ are the charges of ions in solutions. A , B are the Debye-Hückel constant and (r) is the solvated radius.

$$A = 1.824 \cdot 10^6 / (\epsilon T)^{3/2}; \quad B = 50.29 \cdot 10^8 (\epsilon T)^{-1/2}$$

The association constant (K_a) for the reaction of the type:



Is given by the following equation:

$$K_a = \frac{C_{[MX_n]} \gamma_{[MX_n]}}{C_{M^{n+}} \gamma_{M^{n+}} C_{X^-}^n \gamma_{X^-}^n} \quad (9)$$

The values of the triple ion association constant (K_3) were calculated [32] by using the following equation:

$$\frac{\Lambda C^{1/2}}{(1 - \frac{\Lambda}{\Lambda^{\circ}})^{1/2}} = \frac{\Lambda^{\circ}}{(K_a)^{1/2}} + \frac{C \Lambda_3^{\circ}}{K_3 (K_a)^{1/2}} \left(1 - \frac{\Lambda}{\Lambda^{\circ}}\right) \quad (10)$$

Equation 10 was derived by Fuoss and using Walden approximation ($\Lambda = 3\Lambda^{\circ}$), the values of K_3 were calculated and reported in Table 4. The values of the change free energy of association (ΔG_a°) were calculated using the following equation:

$$\Delta G_a^{\circ} = -2.303 RT \log K_a \quad (11)$$

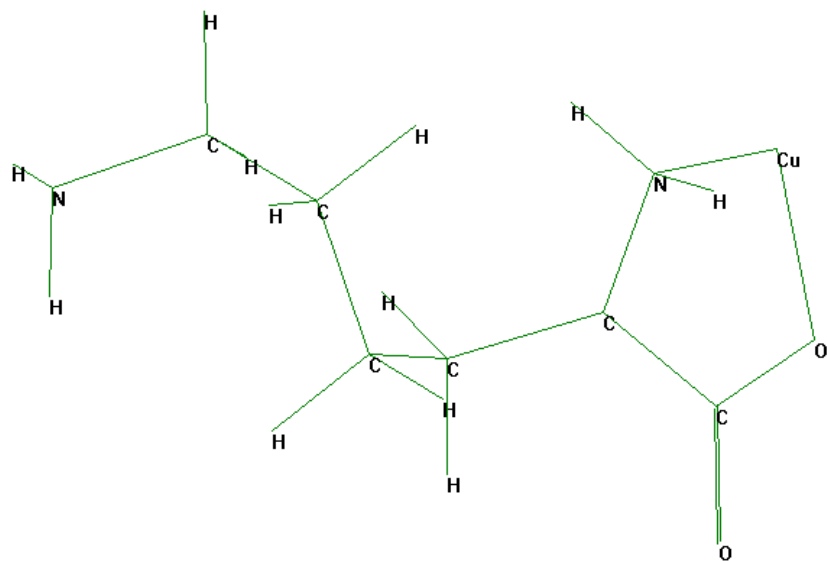
Where, R is the gas constant and T is the absolute temperature.

Table 1. The formation constants (K_f), and the free energy change (ΔG_f°) of the metal cation-amino acid complexes in aqueous solution at 298.15 K

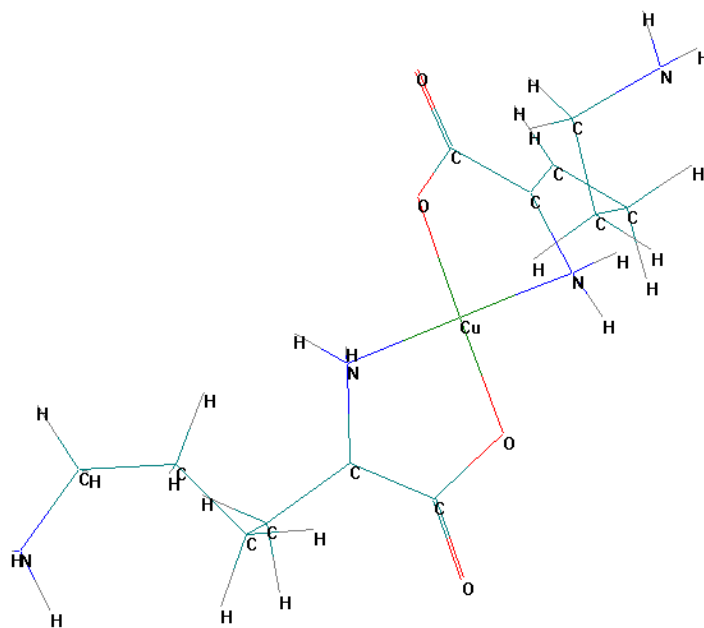
| Metal Cation | L:M | Glycine | | Cysteine | | Lysine | |
|------------------|-----|------------------------------|-------------------------------|------------------------------|-------------------------------|------------------------------|-------------------------------|
| | | K_f (mol/dm ³) | ΔG_f° (kJ/mol) | K_f (mol/dm ³) | ΔG_f° (kJ/mol) | K_f (mol/dm ³) | ΔG_f° (kJ/mol) |
| Mn ⁺² | 1:1 | 14235.060 | -23.3128 | 4050.194 | -20.2487 | 1274.235 | -17.4297 |
| | 2:1 | 10076.410 | -22.4796 | 349.131 | -14.2738 | 522.095 | -15.2547 |
| | 3:1 | 599.998 | -15.5964 | 442.218 | -14.8499 | 229.861 | -13.2549 |
| Ni ⁺² | 1:1 | 834.381 | -16.3972 | 101.604 | -11.6037 | 1947.321 | -18.4636 |
| | 2:1 | 1088.129 | -17.0443 | 689.719 | -16.2052 | 850.730 | -16.4400 |
| | 3:1 | 1285.671 | -17.4507 | 91.473 | -11.1965 | 277.949 | -13.7179 |
| Cu ⁺² | 1:1 | 4557.566 | -20.5364 | 1394.386 | -17.9494 | 2158.077 | -18.7141 |
| | 2:1 | 283.924 | -13.7698 | 691.127 | -16.2151 | 948.835 | -16.7109 |
| | 3:1 | 1008.051 | -16.8585 | 213.501 | -13.2970 | 463.920 | -14.9667 |

Table 2. The enthalpy of formation (ΔH), the volume (V), the molar refraction (R), dipole moment (μ) and polarizabilities (α) of the metal cation- cysteine complexes as calculated applying the semi-empirical PM3 program at 298.15 K

| Metal Cation | Amino acid (Cysteine) | L:M | $-\Delta H$ (kJ/mol) | V (Å ³ /mol) | R (Å ³ /mol) | μ , (C m) | α (Å ³) |
|------------------|-----------------------|-----|----------------------|---------------------------|---------------------------|---------------|----------------------------|
| Mn ⁺² | through S atom | 1:1 | 8.2066 | 369.50 | 24.30 | 8.83 | 9.70 |
| | | 2:1 | 8.7022 | 659.90 | 50.00 | 6.30 | 17.40 |
| | through O atom | 1:1 | 8.2064 | 373.40 | 25.30 | 5.10 | 10.36 |
| | | 2:1 | 8.3293 | 670.40 | 49.20 | 4.40 | 20.00 |
| Ni ⁺² | through S atom | 1:1 | 23.1950 | 433.80 | 24.30 | 7.80 | 9.59 |
| | | 2:1 | 23.6900 | 679.70 | 50.00 | 1.52 | 17.40 |
| | through O atom | 1:1 | 23.6241 | 429.70 | 25.36 | 8.82 | 10.38 |
| | | 2:1 | 23.4319 | 680.80 | 49.24 | 2.44 | 20.04 |
| Cu ⁺² | through S atom | 1:1 | 26.5677 | 376.90 | 24.30 | 4.50 | 9.60 |
| | | 2:1 | 27.0715 | 696.80 | 50.00 | 7.28 | 17.44 |
| | through O atom | 1:1 | 26.5670 | 374.40 | 25.36 | 5.75 | 10.39 |
| | | 2:1 | 26.6830 | 686.50 | 49.24 | 4.32 | 20.05 |



Lysine - Cu⁺² (1:1 L/M) complex



Lysine - Cu⁺² (2:1 L/M) complex

(Scheme 3)

The Walden product ($\Lambda \cdot \eta$) values [32] were calculated for MnCl_2 , NiCl_2 and CuCl_2 in aqueous solution in the absence and in the presence of glycine and lysine amino acids at 293.15 K. The Walden product values as computed from the limiting molar conductance values (Λ), would be informative from the point of view of ion-solvent interactions.

The limiting molar conductance (Λ), the association constant (K_a), the free energy change of association (ΔG_a), the triple ion association constant (K_3), and the Walden product ($\Lambda \cdot \eta$) of MnCl_2 , NiCl_2 and CuCl_2 in aqueous solution in absence and in presence of glycine and lysine at 298.15 K are reported in Table 4.

Table 3. The enthalpy of formation (ΔH), the volume (V), the molar refraction (R), dipole moment (μ) and polarizabilities (α) of the metal cation-amino acid (Glycine and Lysine) complexes as calculated applying the semi-empirical PM3 program at 298.15 K

| Amino acid | Metal Cation | L:M | $-\Delta H$ (kJ/mol) | V ($\text{\AA}^3/\text{mol}$) | R $\text{\AA}^3/\text{mol}$ | μ , (C m) | α (\AA^3) |
|------------|------------------|-----|-------------------------|--------------------------------------|----------------------------------|------------------|--------------------------------|
| Glycine | Mn^{+2} | 1:1 | -0.0632 | 270.5 | 8.70 | 6.40 | 5.10 |
| | | 2:1 | 9.1149 | 465.0 | 17.40 | 1.30 | 10.00 |
| | Ni^{+2} | 1:1 | 23.9861 | 316.4 | 8.70 | 6.10 | 5.10 |
| | | 2:1 | 23.2000 | 459.3 | 17.40 | 1.50 | 10.10 |
| | Cu^{+2} | 1:1 | -27.3350 | 271.8 | 8.70 | 7.80 | 5.10 |
| | | 2:1 | 27.4731 | 461.1 | 17.40 | 7.80 | 10.10 |
| Lysine | Mn^{+2} | 1:1 | 1.9651 | 506.24 | 30.94 | 5.74 | 13.70 |
| | | 2:1 | 11.8840 | 893.15 | 60.06 | 6.79 | 26.54 |
| | Ni^{+2} | 1:1 | 16.9083 | 535.00 | 30.94 | 2.93 | 13.80 |
| | | 2:1 | 22.5080 | 1087.55 | 62.50 | 2.64 | 28.05 |
| | Cu^{+2} | 1:1 | 20.2508 | 504.00 | 30.94 | 6.26 | 13.80 |
| | | 2:1 | 26.3300 | 920.00 | 58.00 | 10.33 | 27.48 |

Table 4. The limiting molar conductance (Λ), the association constant (K_a), the free energy change of association (ΔG_a), the triple ion association constant (K_3), the Walden product ($\Lambda\eta$) and correlation coefficient square (R^2) of MnCl_2 , NiCl_2 and CuCl_2 in aqueous solution in absence and in presence of glycine and lysine at 293.15 K

| Amino acid | Property | MnCl_2 | NiCl_2 | CuCl_2 |
|---|---|---|-----------------|-----------------|
| No one | Λ ($\text{S cm}^2 \text{mol}^{-1}$) | 481.32 | 344.34 | 164.03 |
| | K_a (l mol^{-1}) | 701.734 | 801.375 | 1193.956 |
| | ΔG_a (kJ/mol) | -15.9755 | -16.2992 | -17.2711 |
| | K_3 (l mol^{-1}) | -0.0043 | -0.0039 | -0.0056 |
| | $\Lambda\eta$ ($\text{S cm}^2 \text{mol}^{-1} \text{cP}$) | 4.8006 | 3.4344 | 1.6360 |
| | R^2 | 0.9785 | 0.9550 | 0.9648 |
| | Glycine | Λ ($\text{S cm}^2 \text{mol}^{-1}$) | 492.86 | 378.41 |
| K_a (l mol^{-1}) | | 952.035 | 965.846 | 1418.278 |
| ΔG_a (kJ/mol) | | -16.7191 | -16.7542 | -17.6908 |
| K_3 (l mol^{-1}) | | -0.0050 | -0.0051 | -0.614 |
| $\Lambda\eta$ ($\text{S cm}^2 \text{mol}^{-1} \text{cP}$) | | 4.9157 | 3.7743 | 1.8799 |
| R^2 | | 0.9625 | 0.9363 | 0.9627 |
| Lysine | | Λ ($\text{S cm}^2 \text{mol}^{-1}$) | 944.41 | 778.58 |
| | K_a (l mol^{-1}) | 3015.924 | 3340.170 | 7147.534 |
| | ΔG_a (kJ/mol) | -19.5299 | -19.7789 | -21.6333 |
| | K_3 (l mol^{-1}) | -0.0091 | -0.0096 | -0.0141 |
| | $\Lambda\eta$ ($\text{S cm}^2 \text{mol}^{-1} \text{cP}$) | 9.4195 | 7.7655 | 6.5321 |
| | R^2 | 0.9322 | 0.9339 | 0.9479 |

It was observed that, as the association constant increase, the limiting molar conductance decrease for the studied salts in aqueous medium at 293.15 K in absence and in the presence of the amino acids (Table 4). In the presence of the amino acids, the data in Table 4, indicate that the association constant and the limiting molar conductance of the studied salts in aqueous medium at 293.15 K increase comparing to that in the absence of the amino acids (Fig. 9). This may be due to the complexation of the salts with the amino acids and the expected formation of a charged

complexed ion as in the case of lysine. Also this behavior was reflected from the values of the correlation coefficient square (R^2) of the graphic relation of Λ versus $C^{1/2}$ for the studied transition metal salts in absence and in the presence of glycine and lysine. The correlation coefficient square of the studied transition metal salts in the presence of glycine and lysine was found to be less than that in the absence of glycine and lysine.

The effect of glycine on the association of the studied salts in aqueous medium at 293.15 K

was found to be less than that of lysine (Fig. 9). The less effect of glycine than that of lysine may be due to the chemical structure of each of them (Scheme 1) and the ability of each of them to chelate the transition metal cation. This may be due to the higher formation constant of most glycine-transition metal cation complexes than that of lysine- transition metal cation complexes. This also can be noted from the lower values of the limiting molar conductance of the studied transition metal salts in the presence of glycine than that in the presence of lysine as a result of the expected formation of a charged complexed ion in the case of lysine. Also the correlation

coefficient square of the studied transition metal salts in the presence of glycine was found to be more than that in the presence of lysine as a result of higher formation constant and less association constants in the presence of lysine than in the presence of glycine.

The data in Table 2 also indicate that the association constant of the studied salts in aqueous medium at 293.15 K in the absence and in the presence of glycine and lysine, increase in the following order: $MnCl_2 < NiCl_2 < CuCl_2$. This can be explained depending on the following order of the ionic radius

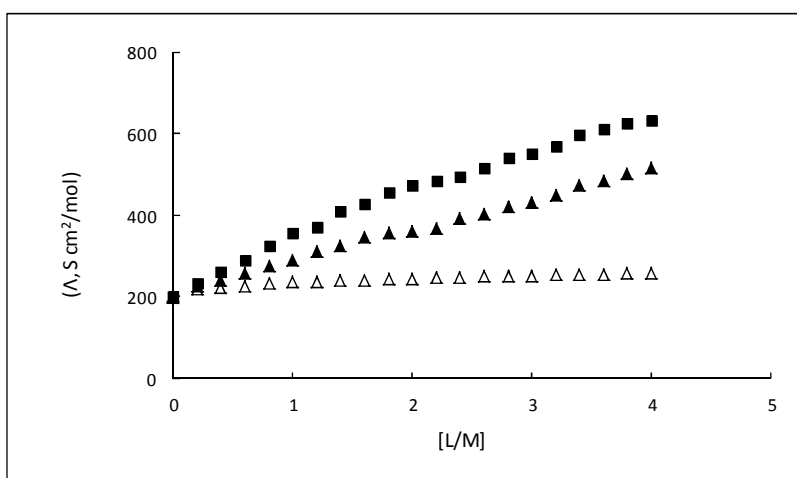


Fig. 1. The molar conductance (Λ) versus the [L/M] ratio for $CuCl_2$ with (■) cysteine, (▲) lysine and (Δ) glycine in aqueous solution at 293.15 K

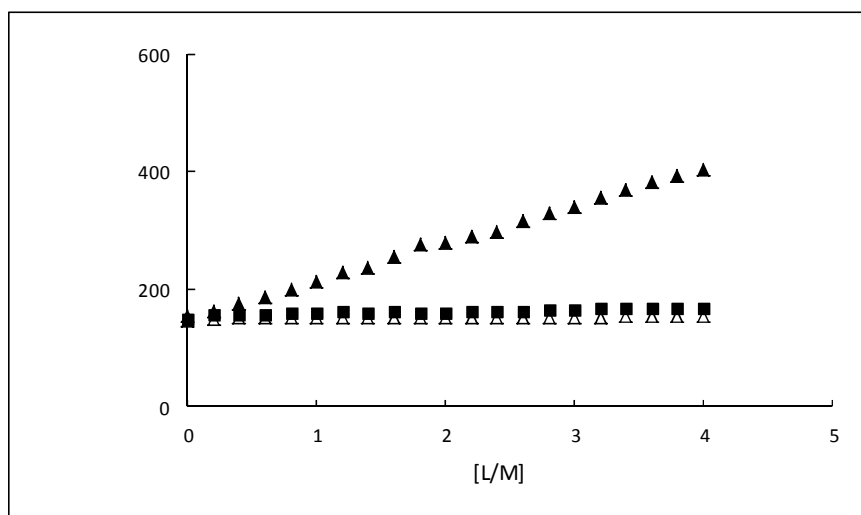


Fig. 2. The molar conductance (Λ) versus the [L/M] ratio for $MnCl_2$ with (■) cysteine, (▲) lysine and (Δ) glycine in aqueous solution at 293.15 K

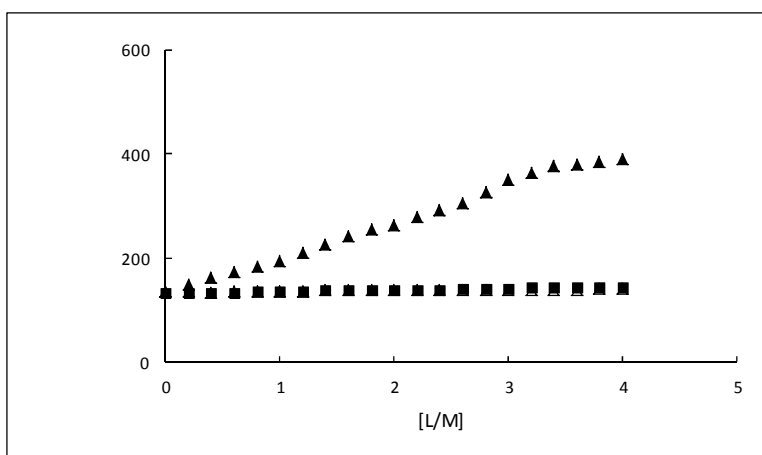


Fig. 3. The molar conductance (Λ) versus the [L/M] ratio for NiCl_2 with (■) cysteine, (▲) lysine and (Δ) glycine in aqueous solution at 293.15 K

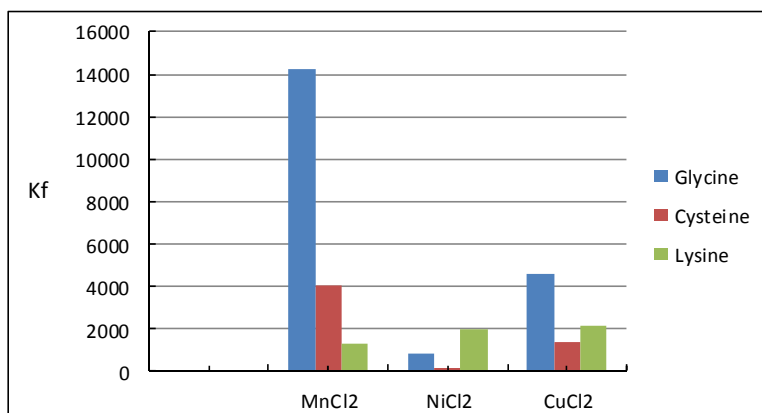


Fig. 4. The formation constants (K_f) for (1:1) [L/M] complex of MnCl_2 , NiCl_2 and CuCl_2 with glycine, cysteine and lysine in aqueous solution at 293.15 K

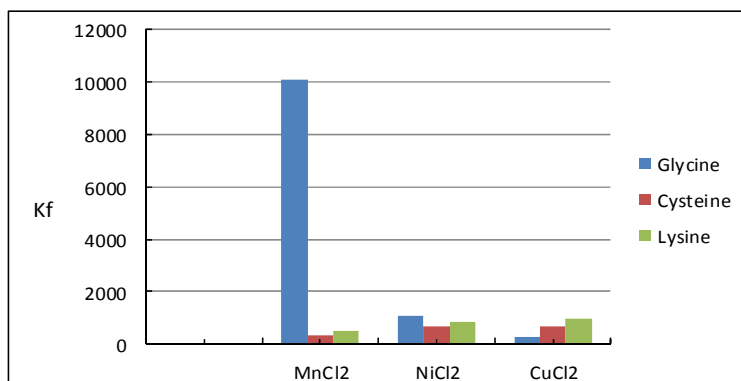


Fig. 5. The formation constants (K_f) for (2:1) [L/M] complex of MnCl_2 , NiCl_2 and CuCl_2 with glycine, cysteine and lysine in aqueous solution at 293.15 K

of the transition metal cation: $\text{Mn}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2}$, association constant decrease. This was whereas the ionic radius increase, the reflected in the values of the correlation coefficient

square of the studied salts in aqueous medium at 293.15 K in the absence and in the presence of glycine and lysine, which increase in the following order: $MnCl_2 < NiCl_2 < CuCl_2$. Also, this was reflected in the limiting molar conductance (Λ) of the studied salts in aqueous medium at 293.15 K in the absence and in the presence of glycine and lysine, which were in the following order: $MnCl_2 > NiCl_2 > CuCl_2$ as a result of the change of the association constants in the order: $MnCl_2 < NiCl_2 < CuCl_2$.

The triple ion ($M^{+2} - 2Cl^- - M^{+2}$) or ($Cl^- - M^{+2} - Cl^-$) association constant (K_3) values in the absence and in the presence of glycine and lysine, were found to be very small values, indicating that this association is negligible or can't be takes place in the studied systems. The data also indicate that the association process of the studied salts in aqueous medium at 293.15 K in the absence and in the presence of glycine and lysine is spontaneous process as indicated from the negative values of the free energy of association (ΔG_a).

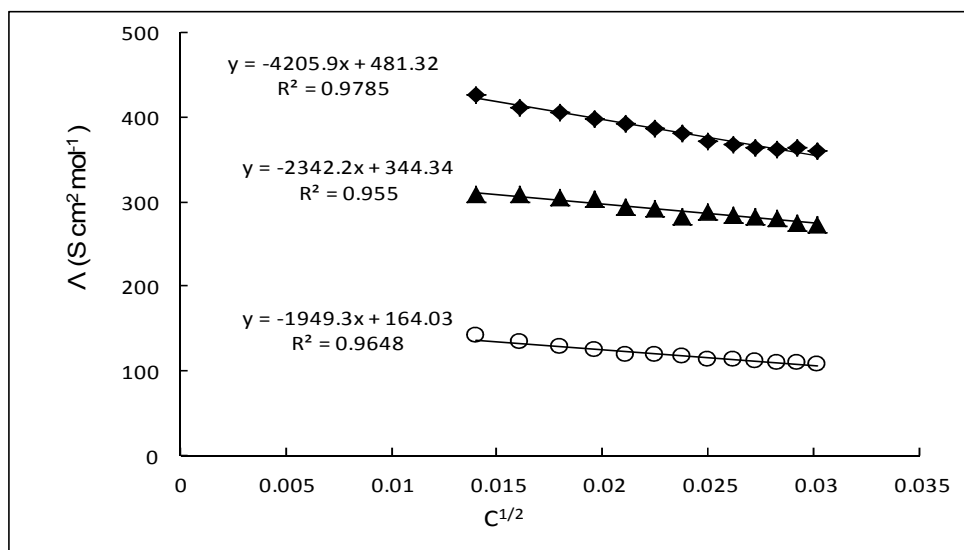


Fig. 6. The molar conductance versus $C^{1/2}$ for (■) $MnCl_2$, (▲) $NiCl_2$ and (○) $CuCl_2$ salts in the absence of glycine and lysine in aqueous solution at 298.15 K

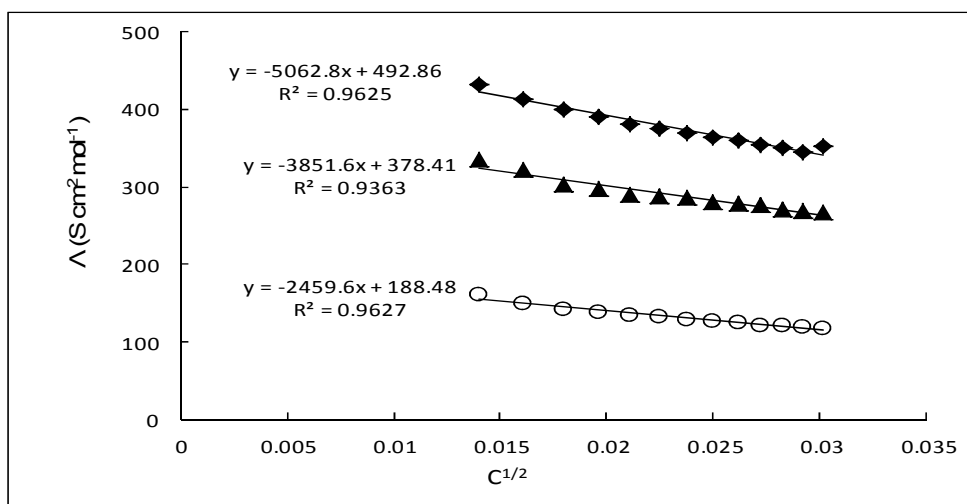


Fig. 7. The molar conductance versus $C^{1/2}$ for (■) $MnCl_2$, (▲) $NiCl_2$ and (○) $CuCl_2$ salts in the presence of glycine in aqueous solution at 298.15 K

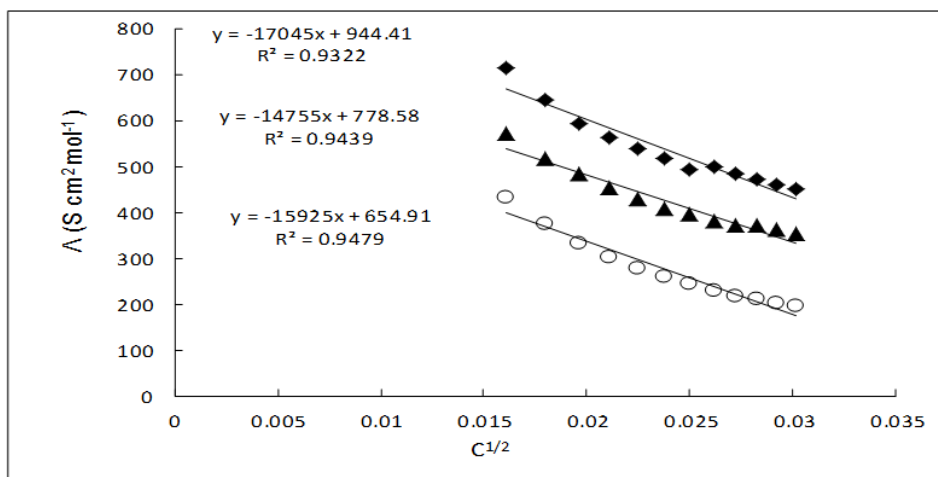


Fig. 8. The molar conductance versus $C^{1/2}$ for (■) $MnCl_2$, (▲) $NiCl_2$ and (○) $CuCl_2$ salts in the presence of lysine in aqueous solution at 298.15 K

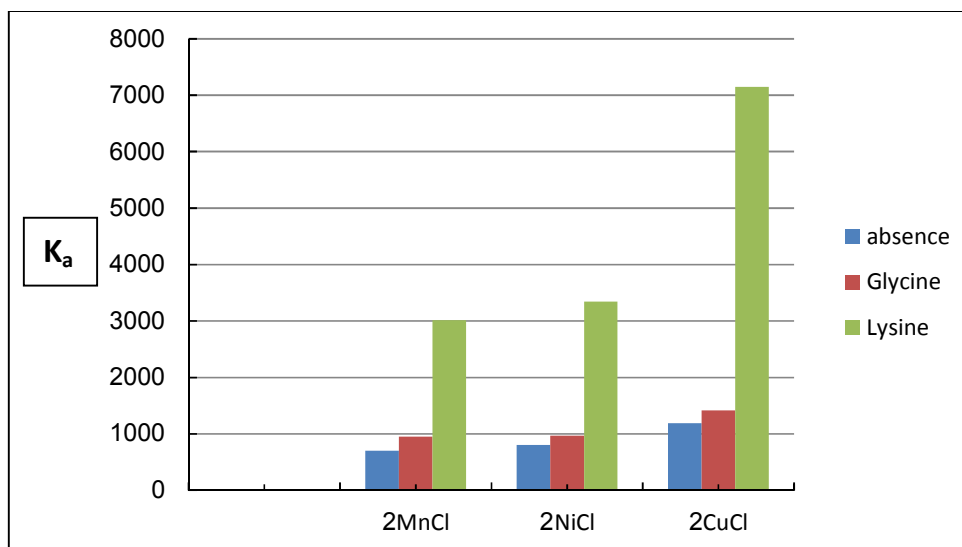


Fig. 9. The association constant (K_a) of $MnCl_2$, $NiCl_2$ and $CuCl_2$ in aqueous solution in absence and in presence of glycine and lysine at 293.15 K

The Walden product ($\Lambda \cdot \eta$) [33] values of the studied salts in aqueous medium at 293.15 K in the absence and in the presence of glycine and lysine were calculated and reported in Table 4. The Walden product ($\Lambda \cdot \eta$) of the studied transition metal salts in the presence of glycine and lysine was found to be more than that in the absence of glycine and lysine as a result of more limiting molar conductance of the salts in presence of the amino acids. Also the Walden product of the studied transition metal salts in the presence of glycine was found to be less than that in the presence of lysine as a

result of higher limiting molar conductance in the presence of lysine that in the presence of glycine.

4. CONCLUSIONS

The complexation reactions between different amino acids (Glycine, L-Lysine, and L-Cysteine) and transition metal cations (Ni^{2+} , Cu^{2+} , and Mn^{2+}) were studied conductometrically in water at 293.15 K. Semi-empirical PM3 calculations were also used to predict the structure of the metal complex. The association constant (K_a) of

MnCl₂, NiCl₂ and CuCl₂ in aqueous solution in the absence and in the presence of glycine and lysine amino acids at 293.15 K were also determined conductometrically. The results indicate that the formation constant of Mn²⁺ and Cu²⁺ with glycine is more in general than that with cysteine and lysine. The results also indicate that the association constant of the studied salts increase in the presence of the amino acids under consideration (glycine and lysine) comparing to that in the absence of these amino acids. The effect of glycine on the association of the studied salts was found to be less than that of lysine. Also the formation and the association processes are spontaneous one.

COMPETING INTERESTS

Authors have declared that no competing interests exist

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