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Potentiometric Studies of the pH Effect on the Coordination Behavior of Citric Acid Complexes with Cu^{2+} and Zn^{2+} in Heterobimetallic Complexes

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دراسة جهدية لتأثير الأس الهيدروجيني *(pH)* على السلوك التناسقي لمعقدات حمض الستريك مع أيوني النحاس الثنائي *(Cu^{2+})* والزنك الثنائي *(Zn^{2+})* في المعقدات ثنائية الفلزات (الغير متجانسة)

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Abstract:
This study investigates the influence of pH on the coordination behavior of citric acid with Cu^{2+} and Zn^{2+} ions in aqueous solution using potentiometric method. Experiments were performed at 25 °C and constant ionic strength (0.1 M KCl) to determine protonation constants and stability constants (log β) of binary and heterobimetallic complexes. The results showed three dissociation steps for citric acid (pKa = 3.2, 4.6, 5.6), with partially deprotonated species (H_2Cit^-, $HCit^{2-}$) being the most active in metal binding between pH 3–6. Copper formed more stable complexes (log β ≈ 9.5) than zinc (log β ≈ 7.5), while the mixed Cu–Zn system exhibited enhanced stability (log β ≈ 14) due to synergistic coordination. Increasing ionic strength reduced complex stability, consistent with the Davies model. Spectroscopic data confirmed the formation of stable Cu^{2+}–citrate and Zn^{2+}–citrate species. Overall, the findings highlight strong pH-dependent complexation and cooperative metal–ligand interactions relevant to bioinorganic and environmental systems.

Keywords: Citric acid; pH effect; Cu–Zn complexes; Potentiometry; ionic strength.

الملخص
تبحث هذه الدراسة في تأثير الرقم الهيدروجيني (pH) على السلوك التنسيقي لحمض الستريك مع أيونات Cu^{2+} و Zn^{2+} في محلول مائي باستخدام تقنية قياس الجهد. أُجريت التجارب عند درجة حرارة 25 درجة مئوية وقوة أيونية ثابتة (0.1 مولار كلوريد البوتاسيوم) لتحديد ثوابت البروتون وثوابت الاستقرار (log β) للمعقدات الثنائية وغير المتجانسة ثنائية المعدن. أظهرت النتائج ثلاث خطوات تفكك لحمض الستريك(pKa = 3.2 ، 4.6، 5.6)، وكانت الأنواع المنزوعة البروتون جزئيًا(H_2Cit^-، $HCit^{2-}$) الأكثر نشاطًا في ربط المعادن بين الرقم الهيدروجيني 3-6. شكّل النحاس معقدات أكثر استقرارًا (log β ≈ 9.5)مقارنةً بالزنك (log β ≈ 7.5) ، بينما أظهر نظام النحاس والزنك المختلط استقرارًا مُحسَّنًا ≈ log β (14)بفضل التنسيق التآزري. وقد أدت زيادة القوة الأيونية إلى انخفاض استقرار المعقد، بما يتوافق مع نموذج Davies. وبشكل عام، تُبرز النتائج وجود معقدات قوية معتمدة على الرقم الهيدروجيني وتفاعلات تعاونية بين المعدن والربيطة، ذات صلة بالأنظمة الحيوية غير العضوية والبيئية.

الكلمات المفتاحية: حمض الستريك؛ تأثير الرقم الهيدروجيني؛ معقدات النحاس والزنك؛ قياس الجهد؛ القوة الأيونية.

Introduction

Citric acid ($C_6H_8O_7$), a naturally occurring tricarboxylic acid, plays a significant role in metal coordination chemistry due to its multiple donor sites, including three carboxylic groups and one hydroxyl group [1]. These functional groups allow citric acid to act as a versatile ligand, forming stable complexes with a variety of metal ions, especially transition metals such as Cu^{2+} and Zn^{2+} [2]. The coordination behavior of citric acid is highly dependent on environmental parameters, notably pH, which influences the ionization state of its donor atoms and, consequently, its binding affinity and complex stability [3].

Potentiometric titrations are well-established techniques for investigating the formation constants, speciation, and structural properties of metal-ligand complexes under varying conditions. This technique offer valuable insight into both thermodynamic stability and kinetic behavior of coordination compounds in aqueous media [4-6].

Copper(II) and zinc(II) ions are of particular interest not only due to their essential biological roles but also for their environmental and industrial relevance. Cu^{2+} tends to form more rigid and planar complexes, while Zn^{2+} often adopts tetrahedral or distorted geometries depending on ligand properties and solution conditions [7,8]. Studying these ions in heterobimetallic systems, where both metals coexist and potentially compete or cooperate in coordination, can yield important insights into synergistic or antagonistic interactions. Heterobimetallic complexes involving Cu^{2+} and Zn^{2+} have been proposed as models for metalloenzymes and as functional materials in catalysis and environmental remediation [9].

Despite the known ability of citric acid to bind individually with Cu^{2+} and Zn^{2+}, fewer studies have systematically examined the formation and stability of heterobimetallic complexes involving both metal ions in the same coordination environment, particularly under varying pH conditions. Investigating such systems provides a deeper understanding of their speciation, stability, and electronic transitions, which are crucial for designing metal-based functional systems in biomedical and environmental applications [10-11].

Therefore, this study aims to explore the effect of pH on the formation and stability of citric acid complexes with Cu^{2+} and Zn^{2+} in heterobimetallic systems using potentiometric method. The findings are expected to contribute to the growing field of mixed-metal coordination chemistry and its applications in aqueous media.

Material and methods

Materials and Reagents

- **Chemicals**:

Citric acid monohydrate (analytical grade), Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), Zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), Potassium hydroxide (KaOH), standard solution (0.1 M), Hydrochloric acid (HCl) for pH adjustment, Potassium chloride (KCl) to maintain ionic strength, Deionized, CO_2-free water for all preparations. All materials were used as purchased with an analytical grade from BDH.

Preparation of Solutions

Stock solutions of citric acid, Cu^{2+}, and Zn^{2+} were prepared at a concentration of 1.0×10^{-2} M. All solutions were standardized using appropriate primary standards. Ionic strength was adjusted and maintained at 0.1 M KCl to reduce ionic strength effects on stability constants.

Potentiometric Measurements

- **Apparatus**:

A thermostated titration cell (25 ± 0.1 °C), a calibrated combined glass pH electrode, and a high-precision digital pH meter.

- **Procedure**:

Titrations were performed under nitrogen atmosphere to exclude CO_2. Titration mixtures were included:

a = Free HCl acid (0.01 M) + KCl (0.09M) (control)

b = a+ citric acid (0.002 M) (ligand)

c = b+ metal ion (0.002 M) (Cu^{2+} or Zn^{2+})

d= b + Cu^{2+} + Zn^{2+} (heterobimetallic system)

KOH (0.1 M) was added incrementally while continuously monitoring the pH.

All experiments were conducted in triplicate, and calibration of electrodes were done daily using three standard buffer solutions at pH 4,7 and 10. Blanks and internal standards were used where appropriate.

- **Data Treatment**:

Protonation constants of citric acid and stability constants of binary and ternary complexes were initially estimated following the Irving–Rossotti procedure from potentiometric data [12]. The final refinement of the stability constants was carried out using the Hyperquad2008 software. Species distribution diagrams were generated using HySS. This allows precise evaluation of complex stability, speciation, and metal–ligand binding affinity.

- **Data Input**:
  - pH vs. volume of titrant data
  - Concentrations of ligand and metal ions
  - Ionic strength (kept constant with 0.1 M KCl)
  - Temperature (25 ± 0.1 °C)

pH-Dependent Speciation Studies

- **Software Modeling**:

Species distribution diagrams (predominant ionic forms vs. pH) were modeled to understand the formation regions of mono-, bi-, and hetero-metallic species.

- Calculated stability constants will help map speciation diagrams, which are crucial for understanding:
  - Metal bioavailability
  - Coordination preferences in mixed-metal environments
  - Applications in environmental remediation and bioinorganic chemistry
- This part of the study serves as a quantitative backbone for interpreting all experimental observations and comparing them with known constants in the literature.

Results and discussion

This section outlines the potential outcome variations and scientific discussion framework based on the experimental methodologies proposed in this study.

pH-Dependent Complexation Behavior

Figure (1) shows three distinct inflection points indicating the dissociation of three carboxyl groups with pKa1 = 3.2, pKa2 = 4.6, and pKa3 = 5.6. These values are consistent with the literature values (3, 4.2, 5.4) [13], (2.9, 4.3, 5.7) [14], confirming the accuracy of the experiment. This behavior is explained by the sequential loss of protons from chemically unstable carboxyl groups due to their varying proximity to the central hydroxyl group. Citric acid shows a significant tendency towards formation of all kinds of complexes with metal ions [15]. The shift of the curve towards a higher pH upon the addition of Cu^{2+} and Zn^{2+} indicates the formation of stable metal complexes that reduce the concentration of free H^{+} ions. This suggests that copper possesses a higher coordination capacity due to its orbital energy(d^9) [7].

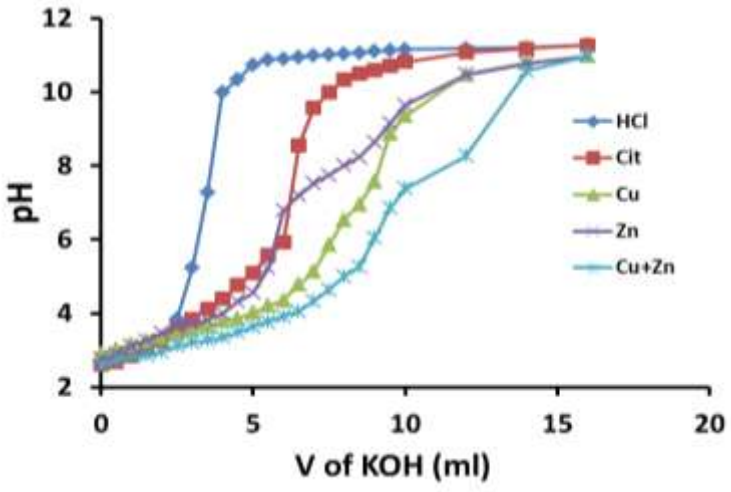

Figure (1): Potential titration curves of citric acid with its metal complexes in an ionic strength of 0.1 M potassium chloride

Proton Species Formation Curves:

The values of ńH (the average number of protons attached to each ligand), determined according to Irving and Rossotti [12], were compiled from the titration curve data using solutions (a) and (b). The proton-ligand dissociation constants were calculated by plotting ńH against pH (Figure 2). The values of pKa1, pKa2, and pKa3 (the dissociation constants of the three protons in Cit^{3-}) are the corresponding pH values for ńH = 0.5, 1.5, 2.5…. The average number of protons attached to each ligand (ńH) at different pH values was calculated using the Irving and Rossotti equations, as shown in Equation (1).

$$\bar{n}H = y + \frac{(V_1 - V_2)(N^o + E^o)}{(V_0 + V_1)\cdot T_c L^o} \ldots\ldots\ldots\ldots 1$$

Where: y = 3 (number of protons available for dissociation in the ligand), V_0 is the initial volume (50 mL), V_1 and V_2 are the volumes of alkali required to achieve the same pH in solution (a) of HCl and solution (b) of HCl + Cit, respectively. TcL_0 is the total concentration of the ligand, N0 is the concentration of the alkali, and E0 is the initial concentration of the free acid.

Figure (2) shows three successive transformation stages from H_3Cit to Cit^{3-} via the intermediate species H_2Cit^- and $HCIt^{2-}$, which are the coordination active species at pH 4–6. The consistency of the interval between the curves confirms the uniformity of proton loss, which is consistent with the literatures data [13], indicating the internal stability of the molecule due to hydrogen bonding.

$H_3Cit \longleftrightarrow H_2Cit^- + H^+$ pKa1 = 3.2

$H_2Cit^- \longleftrightarrow HCit^{-2} + H^+$ pKa2 = 4.6

$HCit^{-2} \longleftrightarrow Cit^{-3} + H^+$ pKa3 = 5.6

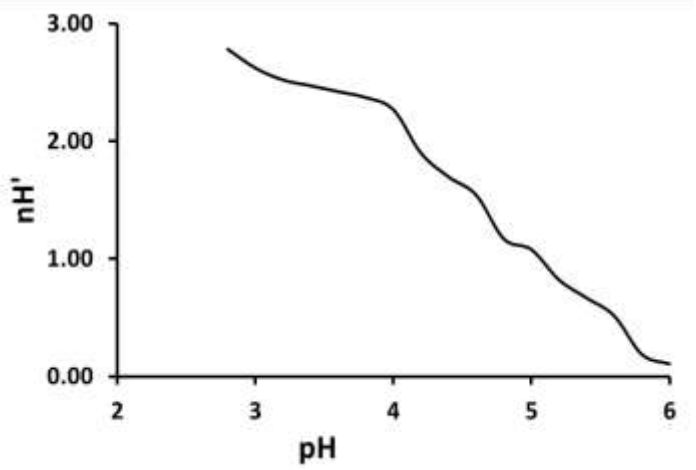

Figure (2): Proton dissociation curve of citric acid in (0.1 M) KCl ionic strength

Metal Complex Formation Curves:

Metric pH titration of the metal ions Cu(II) and Zn(II) was chosen to illustrate their reaction with citric acid. The stability constants of the formed complexes were calculated using the titration curves of the metal-ligand solutions (c), as shown in the titration curve (Figure (1)). The ion titration curves were observed to be shifted to the right of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The significant pH decrease of the metal titration curves relative to the ligand titration curves indicates the formation of strong metal complexes [16,17]. The metal complex formation curves, as shown in Figure 3, were obtained by plotting the average number of ligands attached to each metal ion (n-par) against the free ligand exponent (pL), according to the Irving and Rossotti equations [12].

$$n - par = \frac{(V_3 - V_2)(N^0 + E^0)}{(V_0 + V_1)\bar{n}_H\, TcM^o} \ldots\ldots\ldots\ldots 2$$

$$pL = Log\left[\frac{1 + \beta_1[H^+] + \beta_2[H^+]^2}{(Tcl^0 - \bar{n}TcM^0)} \times \frac{V_0 + V_3}{V_0}\right] \ldots\ldots\ldots 3$$

Where V_1, V_2, and V_3 are the volumes of potassium hydroxide in solutions a, b, and c or d at the same pH, V_0 is the original volume (50 mL) of the mixtures, TcM_0 represents the total concentration of the metal in solution, and β represents the acid-base dissociation constant.

The curves in Figure (3) show that the stability of the copper complexes is higher than that of the zinc complexes, with log β = 9.5 and 7.5, respectively, while it rises to 14 when both ions are present. This increase demonstrates metal-metal synergism resulting from an complementary distribution of coordination centers [18].

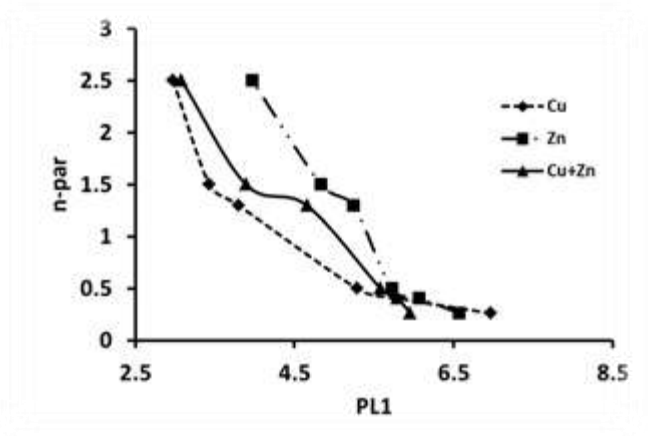

Figure (3): Stability constants formation curve of Cit^{+3} with Cu^{+2}, Zn^{+2} and its mixture (Cu^{+2}+Zn^{+2}) ions in an ionic strength of (0.1 M) KCl

As shown in Table 1, we observe that both copper and zinc ions form complexes with citric acid at molar ratios of 1:1 and 1:2, respectively. On the other hand, the mixture of ions forms complexes at molar ratios of 1:1, 1:2, and 1:3. This is due to the nature of the metal ions.

Table (1): Dissociation and stability constants of citric acid with copper and zinc ions and their mixture, (±) standard deviation, (n=3)

Ion/ System	pKa_1	pKa_2	pKa_3	$logKa_1$	$logKa_2$	$logKa_3$	$Log\beta_n$
Cit^{-3}	3.2±0.1	4.6±0.2	5.6±0.1	—	—	—	
Cu^{2+}—Cit^{-3}	—	—	—	5.5±0.12	4.0±0.2	—	9.5
Zn^{2+} — Cit^{-3}	—	—	—	4.3±0.1	3.2±0.1	—	7.5
Cu^{2+}+ Zn^{2+} — Cit^{-3}	—	—	—	5.6±0.09	4.7±0.2	3.7±0.1	14

The Effect of Ionic strength on stability constants

All potentiometric titrations were performed at a temperature of 25 ± 1.0 °C in a medium with a constant ionic force of 0.1 M KCl. At ionic forces of 0.1, 0.05, 0.01, and 0.006 M, the activity coefficients were calculated using the Davies equation [19]. The apparent and zero stability constants (i.e., at zero ionic force) were corrected ($\log\beta^o$) to deduce the relationship between the corrected stability constants and the ionic force graphically, and to determine the physical direction (the effect of ionic force on stability). We used the Davies equation to estimate the activity coefficients (γ) of the ions in aqueous solutions within the range 0 < I < 0.5 M.

$$\log\gamma = -A.z^2.\left(\frac{\sqrt{I}}{(1+\sqrt{I})} - 0.3.I\right) \ldots\ldots\ldots\ldots\ldots (3)$$

Where: A = 0.509 at 25°C for water, (z) is the ion charge, and I represents the ionic strength of the solution (mol/L). The apparent constants ($\log\beta^o$) are related to the true constant at zero ionic strength ($\log\beta^o$) by the following relationship:

$$\left(\sum log_{reacatnts}\gamma - \sum log_{protucts}\gamma\right) - log\beta_{app} = log\beta^0 \ldots\ldots\ldots\ldots (4)$$

(i. e) $\log\beta^o = \log\beta\_app - \Delta\log\gamma$

The choice of this ionic strength (0.1 M) was not arbitrary, but rather based on several fundamental scientific reasons: In aqueous solutions, the ion concentration does not accurately reflect its true activity due to the electrostatic repulsion between charges. Therefore, a KCl solution with a fixed concentration (0.1 M) is used as a "supporting medium" to stabilize ionic activities and make the measured values of pKa and logβ more realistic and comparable. At very low ionic strength (I < 0.05 M), the effect of ionic interactions becomes significant,

while at I ≈ 0.1 M, the attractive and repulsive forces are balanced, which is the concentration recommended in classical studies of metal coordination reactions in aqueous solutions [20].
In Figure (4), it is observed that the stability constant decreases with increasing ionic strength for both copper and zinc, as well as for the mixed solution. This behavior is consistent with the electrostatic theory of the ionic force effect [19], where increasing the concentration of ions in the medium reduces the effective charges between the ions that make up the complex, thus weakening the attraction between them and consequently decreasing the formation constant (log β).
At every ionic strength value, the copper (Cu) constant is greater than the zinc (Zn) constant. This indicates that copper complexes with citric acid are more stable than zinc complexes, due to copper's higher coherence capacity resulting from its smaller ionic radius and larger effective charge (charge-to-volume ratio)[21,22].
The values for the mixture are significantly higher than the individual values for both copper and zinc, especially at low ionic strengths. This suggests a synergistic effect between the two ions in the presence of the ligand (citric acid), leading to the formation of more stable mixed complexes. As the ionic strength increases, this synergistic effect gradually diminishes due to competition between free ions in solution and a decrease in the strength of electrostatic attraction. The difference between the two values gradually decreases with increasing ionic strength because the inhibitory effect of the solvent and external ions becomes more pronounced at higher ionic strengths.

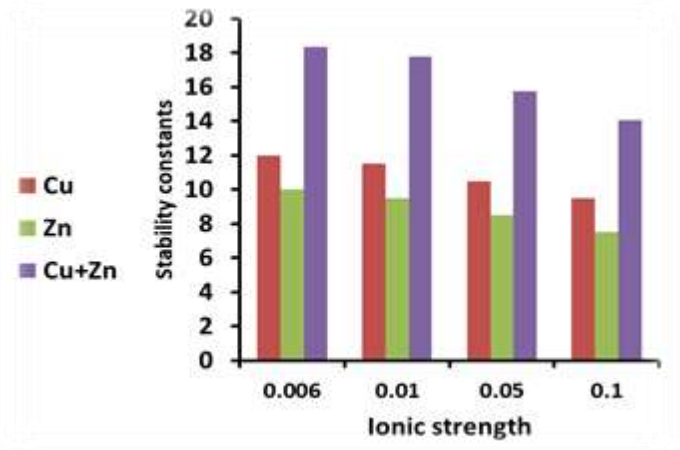

Figure (4): Effect of KCl ionic strength (0.006, 0.01, 0.05, 0.1 M) on the stability constants of citric acid

Species Distribution Variations
The importance of ionic distribution diagrams in this type of study lies in their ability to show the ratios of different chemical species (H_3A, H_2A^-, HA_2^-, A^{-}, etc.) as a percentage of the total concentration of the acid or complex relative to the pH. The species distribution curves for citric acid were obtained by plotting the relationship between the mole fraction of Cit ionic species and pH ranges (Figure 5), where alfa0, alfa1, alfa2, and alfa3 represent the species H_3Cit, and alfa1 represents the major citric acid species (H_3Cit, H_2Cit^-, $HCit^{-2}$, and Cit^{-3}) within the pH range. In Low pH, Citric acid was predominantly in its deprotonated form; hence, its ability to bind metal ions is reduced. The distribution curves show that H_2Cit^- and $HCit^{2-}$ are dominant between pH 3.5 and 6.0, the optimal region for metal complex formation. At pH > 6, Cit^{3-} predominates, reducing its coherence [13].

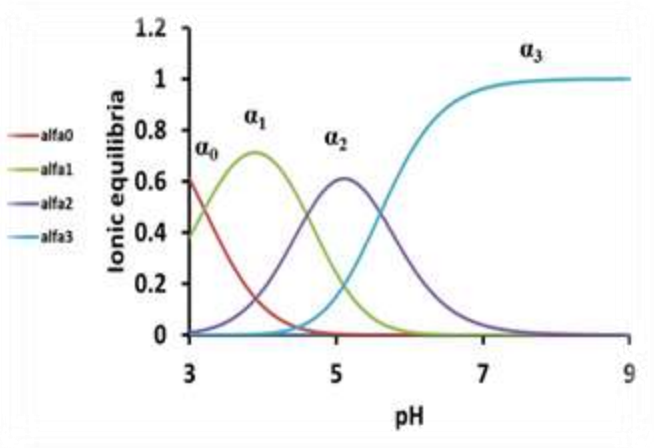

Figure (5): Ionic distribution curve of citric acid at different pH ranges.

The curves in Figures (6,7) illustrate how the form of copper and zinc changes in the presence of citrate (Cit^{-}) with varying pH values. At low pH values, around (3), copper and zinc are mostly present in their free form, $M(Cu^{2+})(Zn^{2+})$, because the citrate is still bound to protons and cannot strongly bond to copper or zinc. When the pH rises to around 4–5, some carboxyl groups in the citrate begin to lose protons, forming complexes of the type ML (Cu–Cit, Zn–Cit), which reach their highest concentration. As the pH rises further (around 5–6), the number of ionized groups in the citrate increases, allowing them to bond to two copper atoms, forming the complex $ML_2Cu\text{-}Cit_2(Zn–Cit^2)$, which becomes the predominant form. At higher pH values, the concentration of these complexes decreases due to the formation of insoluble hydroxide compounds.

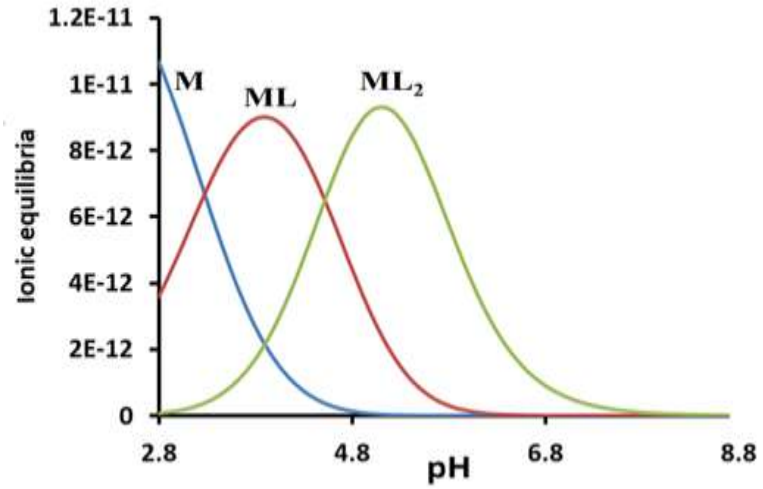

Figure (6): Ionic distribution curve of the citric acid complex with copper ions.

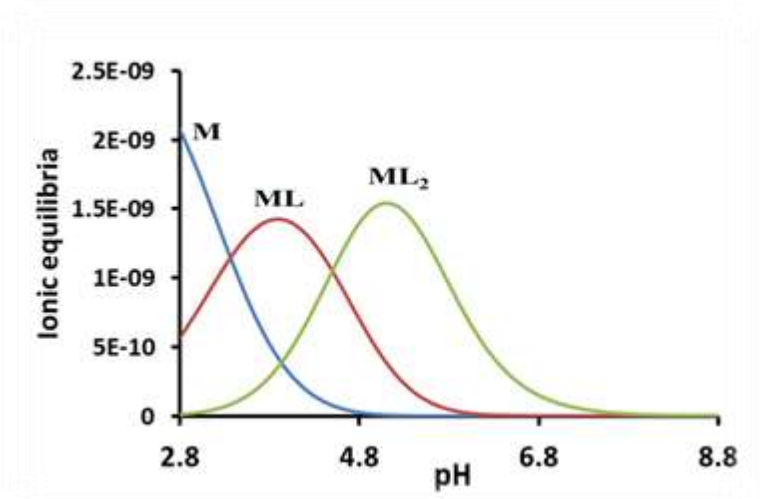

Figure (7): Ionic distribution curve of the citric acid complex with zinc ions

Figure (8) illustrates the distribution of copper isoforms in the presence of both citrate and zinc with varying pH. At low pH values (≈3), the free form of copper, M (Cu^{2+}), predominates because citrate is protonated and not strongly bonded. As the pH rises to approximately 4, the formation of the ML (Cu–Cit) complex begins, and then, at pH between 4 and 5, the formation of ML_2 (Cu–Cit_2) increases, becoming the dominant form in neutral environments. At higher pH (≈6–7), the concentration of ML_2 decreases, and the complex ML_3 (Cu–Cit_3) appears. This complex is more stable in an alkaline environment, where more ionized carboxyl groups are available to coordinate copper. The presence of zinc slightly alters this balance, as it competes with copper for citrate binding. This may reduce the stability of some simpler complexes and increase the formation of polyserotypes such as ML_2 and ML_3 at higher pH values. In summary, the curve illustrates how copper transforms from its free form into increasingly complex compounds with increasing pH, influenced by proton equilibrium and zinc's competition for citrate binding**.**

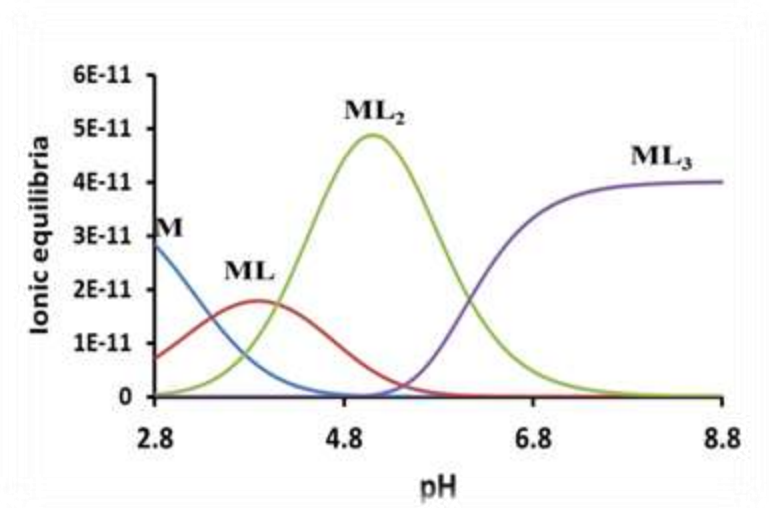

Figure (8): Ionic distribution curve of a mixture of copper and zinc ions with citric acid.

Cu^{2+} was expected to show higher affinity for citric acid due to its electronic configuration and stronger binding capacity. The interplay between the two metal ions may reveal: Competitive binding (one displaces the other) or cooperative binding (formation of heterobimetallic complexes with shared ligands).

To place the present results in context, the obtained stability and speciation data were compared with previously published studies on citrate–metal systems. The comparison highlights the specific contribution of the current work to understanding pH- and ionic-strength-dependent heterobimetallic coordination.

Comparison with previous studies

Earlier investigations on copper–citrate systems have progressively evolved from classical potentiometric studies to structural and computational analyses. Blomqvist & Still (1985) first described polynuclear Cu–Cit species in aqueous media [23], while Pitluck (1987) introduced ion-exchange and atomic absorption techniques to determine binary Cu–Cit stability constants under fixed conditions [24]. Daniele (1988) extended these thermodynamic studies to mixed Cu–M systems (M = Ni^{2+}, Zn^{2+}, Cd^{2+}) without addressing pH or ionic-strength effects [9]. Later, Bastug et al. (2007) focused on temperature-dependent binary complexes [14], and Hamada et al. (2015) characterized Cu_2–Cit dimers using spectroscopic and DFT tools [25]. Only a few studies have addressed zinc–citrate systems in detail. For instance, investigations on Zn(II) complexes with hydroxocarboxylates and mixed Zn–Sn species emphasized the role of supporting electrolytes and ionic strength but neglected pH-dependent equilibria [13]. In contrast, the present work provides a comprehensive pH- and ionic-strength-dependent analysis of Zn^{2+} coordination in both binary and Cu–Zn heterobimetallic systems. The results reveal that Zn^{2+} binds most effectively through the partially deprotonated H_2Cit^- and $HCit^{2-}$ species, and its stability is markedly enhanced by cooperative interaction with Cu^{2+} — a synergistic effect not previously quantified in aqueous citrate chemistry. Furthermore, the present study integrates potentiometric, and computational modeling to examine Cu^{2+}– and Zn^{2+}–citrate systems across variable pH and ionic strength, revealing clear synergistic stabilization ($\log \beta \approx 14$). This provides the first quantitative description of pH-dependent heterobimetallic coordination in aqueous solution.

Conclusion

The study demonstrated that the coordination behavior of citric acid toward Cu^{2+} and Zn^{2+} ions is strongly pH-dependent. Proton dissociation occurs stepwise, and the partially deprotonated species (H_2Cit^-, $HCit^{2-}$) dominate metal binding within pH 3–6. Cu^{2+} forms more stable complexes than Zn^{2+} due to its stronger polarizing power. Mixed-metal systems (Cu–Zn) show synergistic enhancement in complex stability, especially at low ionic strengths, confirming cooperative interactions between the two metal centers.

Compliance with ethical standards

Disclosure of conflict of interest

The author(s) declare that they have no conflict of interest.

References

[1] Ulrich R. Constituents of fruits, 4: Organic acids. In: Hulme AC, editor. *The biochemistry of fruits and their products.* Vol. 1. London: Academic Press; 1970. p. 89–117.

[2] Martell AE, Smith RM. *Critical stability constants.* Vol. 1. New York: Plenum Press; 1974. p. 135.

[3] Pedada SR, Bathula S, Vasa SSR, Charla KS, Gollapalli NR. Micellar effect on metal-ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with citric acid. *Bull Chem Soc Ethiop.* 2009;23(3):.
[4] Irving HM, Miles MG, Pettit LD. A study of some problems in determining the stoicheiometric proton dissociation constants of complexes by potentiometric titrations using a glass electrode. *Anal Chim Acta.* 1967;38:475–88.
[5] Martell AE, Hancock RD. *Metal complexes in aqueous solutions.* New York: Springer Science & Business Media; 2013.
[6] Li M, Zinkle SJ. *Physical and mechanical properties of copper and copper alloys.* 2012.
[7] Kusmariya BS, Tiwari A, Mishra AP, Naikoo GA. Theoretical and experimental studies of Cu(II) and Zn(II) coordination compounds with N,O donor bidentate Schiff base ligand containing amino phenol moiety. *J Mol Struct.* 2016;1119:115–23.
[8] Garcia MCF. *Bacterial nanocellulose biocomposites and hydroxyapatite with cationic substitution by Mg^{2+}, Cu^{2+}, Zn^{2+} and Sr^{2+} for bone regeneration.* 2022.
[9] Daniele PG, Ostacoli G, Zerbinati O, Sammartano S, De Robertis A. Mixed metal complexes in solution. Thermodynamic and spectrophotometric study of copper(II)-citrate heterobinuclear complexes with nickel(II), zinc(II) or cadmium(II) in aqueous solution. *Transit Met Chem.* 1988;13(2):87–91.
[10] Bertrand B, Citta A, Franken IL, Picquet M, Folda A, Scalcon V, et al. Gold(I) NHC-based homo- and heterobimetallic complexes: synthesis, characterization and evaluation as potential anticancer agents. *J Biol Inorg Chem.* 2015;20(6):1005–20.
[11] Amico P, Daniele PG, Ostacoli G, Arena G, Rizzarelli E, Sammartano S. Mixed metal complexes in solution. Part II. Potentiometric study of heterobinuclear metal(II)-citrate complexes in aqueous solution. *Inorg Chim Acta.* 1980;44:L219–L221.
[12] Irving HM, Rossotti HS. The calculation of formation curves of metal complexes from pH titration curves in mixed solvents. *J Chem Soc (Resumed).* 1954;2904–10.
[13] Zabiszak M, Nowak M, Taras-Goslinska K, Kaczmarek MT, Hnatejko Z, Jastrzab R. Carboxyl groups of citric acid in the process of complex formation with bivalent and trivalent metal ions in biological systems. *J Inorg Biochem.* 2018;182:37–47.
[14] Bastuğ AS, Göktürk S, Şişmanoğlu T. 1:1 Binary complexes of citric acid with some metal ions: stability and thermodynamic parameters. *Rev Inorg Chem.* 2007;27(1).
[15] Aoyagi N, Palladino G, Nagasaki S, Kimura T. Optical properties of trinuclear citrate complexes containing 4f and 5f block metals. *Bull Chem Soc Jpn.* 2018;91(6):882–90.
[16] Olin Å, Wallién B. Determination of citrate by potentiometric titration with copper(II) and a copper ion-selective electrode. *Anal Chim Acta.* 1983;151:65–75.
[17] Irving HMNH, Williams RJP. Order of stability of metal complexes. *Nature.* 1948;162(4123):746–7.
[18] Drago RS, Long JR, Cosmano R. Metal synergism in the coordination chemistry of a metal-metal bonded system: tetrakis(μ-butyrato)-dirhodium(II). *Inorg Chem.* 1981;20(9):2920–7.
[19] Davies CW. The extent of dissociation of salts in water. Part VIII. An equation for the mean ionic activity coefficient of an electrolyte in water, and a revision of the dissociation constants of some sulphates. *J Chem Soc (Resumed).* 1938;2093–8.
[20] Baes CF Jr, Mesmer RE. *Thermodynamics of cation hydrolysis. Am J Sci.* 1981;281(7).
[21] Capone S, De Robertis A, De Stefano C, Sammartano S. Formation and stability of zinc(II) and cadmium(II) citrate complexes in aqueous solution at various temperatures. *Talanta.* 1986;33(9):763–7.
[22] Cigala RM, Crea F, De Stefano C, Foti C, Milea D, Sammartano S. Zinc(II) complexes with hydroxocarboxylates and mixed metal species with tin(II) in different salts aqueous solutions at different ionic strengths: formation, stability, and weak interactions with supporting electrolytes. *Monatshefte für Chemie.* 2015;146(4):527–40.
[23] Blomqvist K, Still ER. Solution studies of systems with polynuclear complex formation: copper(II) and cadmium(II) D-gluconate systems. *Anal Chem.* 1985;57(3):749–52.
[24] Pitluck MR, Pollard BD, Haworth DT. Determination of stability constants of a copper/citric acid complex by ion-exchange chromatography and atomic absorption spectrometry. *Anal Chim Acta.* 1987;197:339–42.
[25] Hamada YZ, Cox R, Hamada H. Cu^{2+}-citrate dimer complexes in aqueous solutions. *J Basic Appl Sci.* 2015;11:583–9.

