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PH-Driven Coordination Behaviour and Speciation Modelling of Copper and Zinc Ions in a Mixed Citric–Succinic Acid System

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Abstract:

The protonation and complexation behaviour of the mixed-ligand system composed of citric (Cit) and succinic (Succ) acids with mixed-metal ions of Cu^{2+} and Zn^{2+} was investigated potentiometrically at 25 °C and an ionic strength of 0.1 M KCl. The combined ligand system (Cit + Succ) exhibited apparent pKa values (3.6, 4.2, 5.2, 6.0), reflecting mutual protonation shifts arising from overlapping carboxylate equilibria. Complexation results showed that Cu^{2+} forms significantly more stable binary complexes ($\log \beta = 11.7$) than Zn^{2+} ($\log \beta = 9.4$). When both metal ions coexist, the overall stability of the mixed-metal system reached a remarkably high value ($\log \beta = 22.9$). Calculation of the synergism index ($\Delta\log\beta$) revealed strong antagonism for the ternary complexes involving a single metal bound simultaneously to Cit and Succ, particularly for citrate, which exhibited pronounced destabilisation in the presence of both Cu^{2+} and Zn^{2+}. In contrast, succinate showed mild positive synergism, especially under conditional pH conditions. Most notably, the full mixed system (Cu + Zn with Cit + Succ) displayed a substantial positive $\Delta\log\beta$ (+1.8), corresponding to a 63-fold enhancement in stability. This indicates that the observed cooperative behaviour arises not from citrate acting as a central binding platform, but from a heterometallic–heteroligand organisation in which succinate favours complementary coordination while citrate contributes only selectively. Species-distribution analysis supports the presence of stabilised heterometallic arrangements rather than classical central–peripheral ligand partitioning.

Keywords: Citric Acid, Succinic Acid, Mixed Metal Complexes, Potentiometric.

سلوك التنسيق المُوجه بالاس الهيدروجيني ونمذجة التكوين لأيونات النحاس والزنك في نظام احماض الستريك-السكسينيك المختلط

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الملخص

تم دراسة سلوك البروتونات وتكوين المعقدات لنظام الليجند المختلط، المكوَّن من حمضي الستريك (Cit) والسكسينيك (Succ)، مع أيونات معدنية مختلطة من Cu^{2+} وZn^{2+}، بطريقة المعايرات الجهدية عند درجة حرارة 25 درجة مئوية وقوة أيونية 0.1 مولار من كلوريد البوتاسيوم. أظهر نظام الليجند المختلط (Cit + Succ) قيم pKa ظاهرة (3.6، 4.2، 5.2، 6.0)، مما يعكس انزياحات البروتونات المتبادلة الناتجة عن تداخل توازنات الكربوكسيلات. أظهرت نتائج تكوين المعقدات أن Cu^{2+} يُشكِّل معقدات ثنائية أكثر استقرارًا بشكل ملحوظ ($\log \beta = 11.7$) من Zn^{2+} ($\log \beta = 9.4$). عند تواجد أيوني المعدن، يصل الاستقرار الكلي لنظام المعادن المختلطة إلى قيمة عالية بشكل ملحوظ ($\log \beta = 22.9$). كما كشف حساب مؤشر التآزر ($\Delta\log\beta$) عن تضاد قوي للمركبات الثلاثية التي تتضمن معدنًا واحدًا مرتبطًا في آنٍ واحد بـ Cit و Succ، وخاصةً السترات، التي أظهرت زعزعة استقرار واضحة في وجود كلٍّ من Cu^{2+} و Zn^{2+}. في المقابل، أظهر السكسينات تآزرًا إيجابيًا معتدلًا، خاصةً في ظل ظروف الرقم الهيدروجيني المشروطة. والجدير بالذكر أن النظام المختلط الكامل (Cu + Zn مع Cit + Succ) أظهر $\Delta\log\beta$ إيجابيًا كبيرًا (+1.8)، مما يتوافق مع زيادة في الاستقرار بمقدار 63 ضعفًا. يشير هذا إلى أن السلوك التعاوني الملحوظ لا ينشأ من عمل السترات كمنصة ارتباط مركزية، بل من

تنظيم غير متجانس معدني-غير متجانس، حيث يُفضّل السكسينات التنسيق التكميلي بينما يُساهم السترات بشكل انتقائي فقط. يدعم تحليل توزيع الأنواع وجود ترتيبات غير متجانسة معدنية مستقرة بدلًا من تقسيم مركزي-محيطي تقليدي.

الكلمات المفتاحية: حمض الستريك، حمض السكسينيك، معقدات معدنية مختلطة، معايرة جهدية.

Introduction

Organic acids such as citric and succinic acids play key roles in natural chelation, metal transport, and buffering processes in aqueous systems. Their ability to form stable complexes with transition metals like Cu^{2+} and Zn^{2+} has been extensively documented [1,2].

Previous studies have extensively investigated the coordination behaviour of succinic acid with transition-metal ions such as Cu (II), Zn (II), and Ni (II) [3,4], as well as that of citric acid with various metals [5-7]. However, the combined system involving both citric and succinic acids has not been systematically explored. The coexistence of two polycarboxylic acids can induce either synergistic or competitive effects in metal binding, potentially altering the overall stability and proton-dissociation behaviour of the mixed system [8].

Recent studies have revisited such systems using modern computational and potentiometric tools to understand cooperative binding and heterometallic complex formation [9-11]. Mixed-ligand systems are particularly relevant for environmental and biological chemistry, as they model realistic multicomponent matrices found in soils and biological fluids, as a huge number of ligands are likely to compete for metal ions in those systems [12].

Therefore, this study aims to investigate the mixed-ligand complexation of citric and succinic acids with Cu (II) and Zn (II) under controlled ionic strength and temperature. The research provides new insight into the cooperative and competitive interactions between ligands in multi-acid environments, contributing to the understanding of natural chelation processes, biological metal transport, and industrial wastewater treatment involving Cu and Zn.

Methods

Materials and Reagents

Succinic acid and citric acid (analytical grade), Zinc (II) nitrate hexahydrate ($Zn\ (NO_3)_2{\cdot}6H_2O$), Copper (II) nitrate trihydrate ($Cu\ (NO_3)_2{\cdot}3H_2O$), Hydrochloric acid (HCl), Potassium hydroxide (KaOH), standard solution (0.1 M), for pH adjustment, Potassium chloride (KCl) to maintain ionic strength, Deionized, CO_2-free water for all preparations.

Preparation of Solutions

Stock solutions of succinic and citric acids were prepared at a concentration of 0.1 M, while Zn^{2+}, and Cu^{2+}ions were prepared at a concentration of 0.05 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 = HCl acid (0.01M) +KCl(0.09M) (control)
b = a+ succinic acid (1.0×10^{-3}M) (first ligand)
c = a+ citric acid (1.0×10^{-3}M) (second ligand)
d = a+ succinic acid (1.0×10^{-3}M) + citric acid (1.0×10^{-3}M) (mixed ligand)
e = b+ metal ion (1.0×10^{-3}M) (Cu^{2+} or Zn^{2+})
f = b + Cu^{2+} + Zn^{2+} (heterobimetallic system)

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

Data Treatment:

Protonation constants of succinic acid and stability constants of binary and ternary complexes were calculated initially by Irving and Rossotti equations [13], then using Hyperquad2008 software [14]. Species distribution diagrams were generated using Hyperquad Simulation and Speciation (HySS) [15]. Species distribution diagrams (predominant ionic forms vs. pH) were modeled to understand the formation regions of mono-, bi-, and hetero-metallic species.

Reproducibility and Quality Control

All experiments were conducted in triplicate. Calibration of electrodes were done daily by 4, 7, 10 buffer solutions.

Results And Discussion

Titration curves and proton species formation:

Measurements were performed in an ionic neutral aqueous medium (0.1 M KCl) at 25°C to ensure the stability of ionic activities and minimize the effects of charge on chemical equilibrium. Figure (1) shows a series of titration curves reflecting the behaviour of the acids (succinic and citric) and their complexes with copper and zinc under the same salt conditions (0.1 M KCl, 25°C). Inflection points and slope regions are interpreted as follows:

The curves of Succ and Cit show clear inflection points that correspond to the pKa values of the individual acids (Succ: pKa ≈ 4.6 and 5.2; Cit: pKa ≈ 3.2, 4.6, 5.6) as listed in table (1) and from our previously published work [4,5]. The flattened regions between the inflection points represent buffer regions where the acid and its bases share the protons in solution, helping to confirm the given pKa values.

The curve of Succ + Cit (the mixture) shows overlapping in the inflection points and an extension of the proton dissociation regions because the presence of a polycarboxylic ligand and a hydroxyl group adds further apparent dissociation steps.; this explains why the mixture registers an apparent pKa (3.6, 4.2, 5.2, 6.0) that is slightly different from the individual acids, the result is due to ionic interference and the combined effects of the carboxyl and hydroxyl groups on the acid bands.

Cu and/or Zn addition curves: The addition of metal ions alters the shape of the curves through the consumption of some protons in the formation of metal-ligand complexes. This shifts the point of the curve to different pH values and changes the derived amplitude curves. Ideally, observing a decrease in the heights of some turns or the appearance of new turns indicates the stepwise formation of protonated or metallized complexes and confirms the numerical values of the stability constants (logKa) for the complexes as shown in Table (1).

Chemical conclusions: The addition of Cu^{2+} and Zn^{2+} clearly affects the titration behaviour, it delays proton release. It leads to the formation of complexes that affect the apparent dissociation constants of the acids. Mixed complexes (Cit + Succi + Cu + Zn exhibit more complex behaviour, possibly due to the presence of multiple equilibria between mono-, di-, and tertiary complexes. The order of stability of the complexes: $Cu^{2+} > Zn^{2+} >$ Without metals.

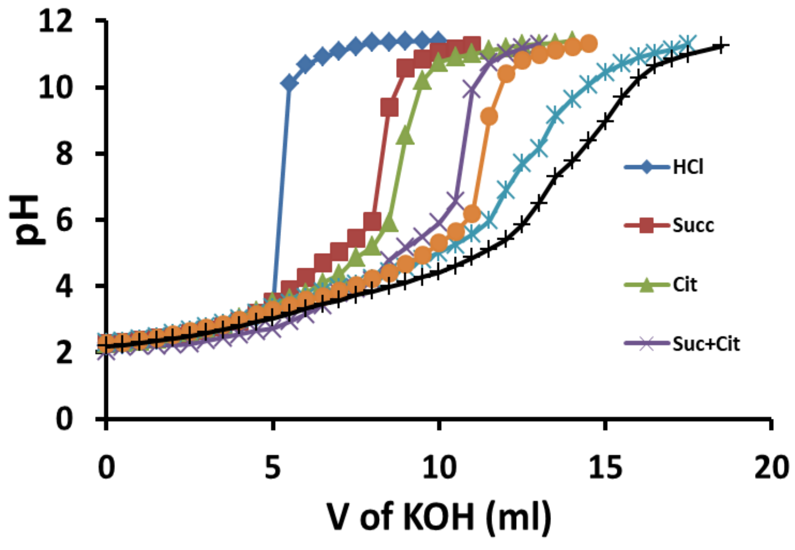

Figure 1. Potential titration curves of citric and succinic acids and their mixture with the metal ions of copper and zinc and their mixture at an ionic strength of 0.1 M KCl

Proton Mixture Curve

Figure (2) illustrates how the proton states are distributed across mixed ligand as pH changes: Inflection points at the corresponding pKa indicate the loss of a specific proton from a functional group (e.g., the first proton of Cit is lost at ≈ 3.2). The mixture curve shows that the sum of the periods during which protons are lost is more extended and closer together than for single ligands; this suggests the overlap of carboxyl/hydroxyl groups that modify each other's acidic capacities through substitution and electron-charge effects. The gradual increase in the total number of fragmented protons reflects each successive pKa (three for Cit and two for Succ). When these are combined, we see four apparent points of the mixture, as recorded in Table (1) (3.6, 4.2, 5.2, 6.0)—which indicates apparent changes in the stability of the acidic points in the presence of the other ligand. This has a direct effect on the binding of metal ions because the state of proton deposition determines the available binding site for the metal.

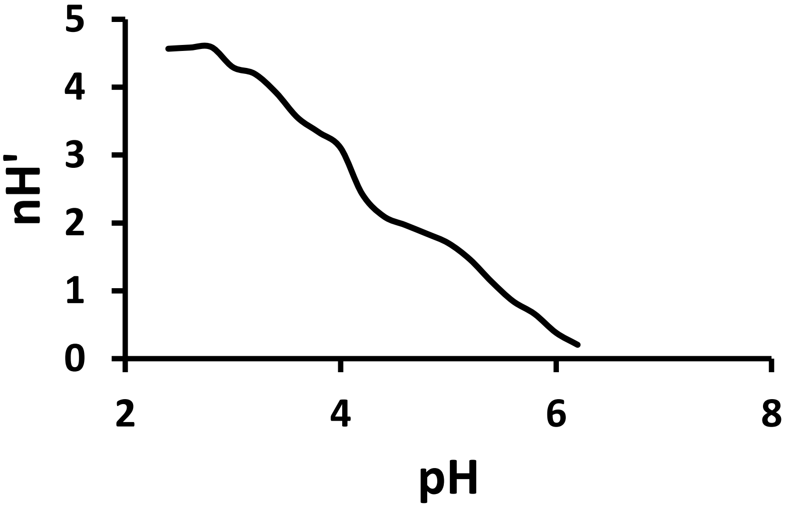

Figure 2. Proton dissociation curve for the acid mixture (Cit+Succ)

Formation of metal complexes

Figure 3 presents the variation of the average number of ligand molecules bound per metal ion (n-par) as a function of pL (−log [Lfree]) for the Cu (II), Zn (II), and mixed Cu–Zn systems with the Cit–Succ ligand mixture. The n-par–pL profile provides a direct measure of the extent of metal–ligand association and allows comparison of binding affinities without requiring explicit stability constants.

The Zn (II) system shows the lowest n-par values across the entire pL range, reaching only about one ligand per metal ion at high ligand concentrations and decreasing steadily as pL increases. This behaviour indicates that Zn (II) forms relatively simple complexes, predominantly of the ML type, and exhibits moderate affinity toward the Cit–Succ mixture. The smooth, gradual decline in the curve suggests predictable and non-cooperative binding dominated by single-step complexation.

In contrast, the Cu (II) system displays higher n-par values (≈1–1.2 at low pL), reflecting its stronger coordinating ability relative to Zn (II). The curve exhibits a distinct inflection around pL ≈ 5, characteristic of stepwise complex formation in Cu (II) systems. This transition implies the existence of multiple coordination species (e.g., ML, MHL or ML_2) and highlights the greater structural flexibility and binding strength of Cu (II) with multifunctional ligands such as citrate and succinate.

The mixed Cu–Zn system shows the most pronounced behaviour, with n-par values approaching four ligand molecules per metal at low pL—significantly higher than either metal alone. The elevated position of the Cu+Zn curve demonstrates a clear cooperative effect, where the simultaneous presence of both metal ions enhances ligand uptake and promotes the formation of heterometallic species. The broad decrease in n̄ with increasing pL indicates that these highly coordinated structures gradually dissociate as the concentration of free ligand decreases, consistent with the expected ligand-driven stability of mixed-metal complexes.

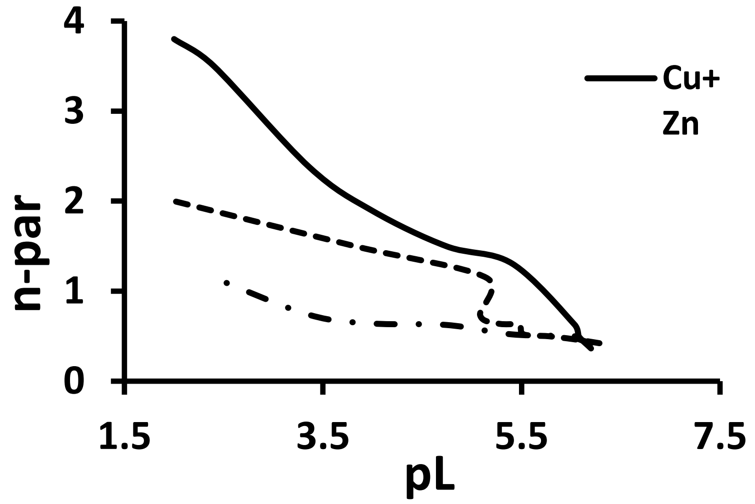

Figure 3. Stability constant formation curve for complexes of the Citric acid mixture (Cit^{-3}) with copper and zinc ions and their combination.

The dissociation constants (pKa) were determined for both citric acid (Cit^{-3}) and succinic acid (Succ^{-2}) as previously reported [4,5], in addition to the individual stability constants (log K_n) for the resulting complexes with copper and zinc ions individually and in combination, and with the same acid mixture.

The measured values in Table 1 for the dissociation constants of the mixture (pKa_1 = 3.6, pKa_2 = 4.2, pKa_3 = 5.2, pKa_4 = 6.0) showed a slight deviation from the individual values for each acid (Cit: 3.2, 4.6, 5.6; Succ: 4.6–5.2), indicating reciprocal protonation between the carboxyl groups of both acids. This effect is attributed to the formation of a network of hydrogen bonds between the molecules, which modifies the electronic environment around the proton-donating groups, a phenomenon known as acidic synergism [10]. Regarding metallic coordination, the results showed that the individual stability constants (log K_n) for the copper and zink complexes with the mixture, the values are higher than those for single acids as previously reported [4,5], suggesting the presence of coordination synergism resulting from the participation of both citric and succinic carboxyl groups in the bonding process [16]. This synergy allows for the formation of more stable complexes due to the formation of complementary ionic and coordination bonds in a more balanced three-dimensional environment.

When the two metal ions are present together (Cu^{2+} + Zn^{2+}), the log Ka1 value increases to 6.1, and subsequent values to 4.7, 3.4, and 2.4, reflecting a cooperative interaction between the metals. This effect can be explained by two complementary mechanisms: the occurrence of a reciprocal coordination distribution where each metal alternates at different bonding sites within the carboxyl structure, and the enhancement of overall stability through reciprocal polarizing effects between the two ions [10]. The high overall log β value (≈ 22.9) compared to the individual values (Cu: 11.7, Zn: 9.4) indicates the formation of a more stable double complex, consistent with the concept of metal-metal synergism [16]. Although the mixed system contains both Cu^{2+} and Zn^{2+}, the stability constants clearly show that copper is the preferred metal ion, as its apparent mixed ligand constant (logβ = 11.7) is significantly higher than that of zinc (logβ = 9.4). This indicates that copper occupies the ligand sites more efficiently under the same experimental conditions.

Table 1. of dissociation and stability constants for a mixture of citric and succinic acids with their metal complexes, (±) standard deviation

ion / system	**pKa1**	**pKa2**	**pKa3**	**pKa4**	**logKa1**	**logKa2**	**logKa3**	**logKa4**	**LogB$_n$**
Cit^{-3}	3.2±0.1	4.6±0.2	5.6±0.1	—	—	—	—	—	
Succ^{2-}	4.6±0.2	5.2±0.1	—	—	—	—	—	—	
Cit^{-3} + Succ^{2-}	3.6±0.1	4.2±0.1	5.2±0.2	6.0±0.1	—	—	—	—	
Cu^{2+}	—	—	—	—	5.8±0.1	3.8±0.2	2.1±0.1	—	11.7
Zn^{2+}	—	—	—	—	5.4±0.1	4.0±0.1	—	—	9.4
Cu^{2+} + Zn^{2+}	—	—	—	—	6.1±0.2	4.7±0.1	3.4±0.1	2.4±0.2	22.9

Enhanced stability" (or synergy)

There is a simple and widely used method for measuring "enhanced stability" (or synergy) in ligand mixtures [17]: calculating the difference between the configuration constant of the ternary compound (metal + ligand 1 + ligand 2) and what would be expected if each ligand behaved independently. A positive result indicates synergy;

a zero result indicates normal "additive" activity; and a negative result indicates competition/inhibition. The formula and concepts are as follows:
The cumulative configuration constant of the ternary compound is denoted by β_{111}, i.e., the effector:

$$M + L_1 + L_2 \rightleftharpoons ML_1L_2$$

The binary constants of the monomeric compounds with each ligand are: β_{101} for compound ML_1 and β_{011} for compound ML_2. β is usually given as a cumulative value.
The "enhancement/synergism" equation:
A common indicator is the logarithmic difference [17]:

$$\Delta log\beta = log\beta_{111} - (log\beta_{101} + \beta_{011}) \ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Or, alternatively, the enhancement ratio:

$$E = \frac{\beta_{111}}{\beta_{101}\beta_{011}} \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$logE = \Delta log\beta \ldots\ldots\ldots\ldots\ldots.(3)$$

To resolve the antagonism issue in our system, we used the logarithmic difference index [19].

$$\Delta log\beta = \sum log\beta_{individual} - log\beta_{mixed} \ldots\ldots\ldots\ldots\ldots..(4)$$

Where:

$\log\beta_{mixed}$ is the overall stability constant of the mixed (ternary or heterometallic) complex. $\sum\log\beta_{individual}$ is the sum of the stability constants of the corresponding binary complexes.

In the case of one metal + two ligands (Cit and Succ), Δlogβ is calculated by comparing the cumulative formation constant of the tertiary complex with the sum of the binary formation constants. The results show that both copper and zinc give large negative values (Cu: Δlogβ = −4.10, Zn: Δlogβ = −3.00), clearly indicating antagonism—that is, attempting to bond both ligands to the same metal center reduces the actual stability compared to the expected combination.

In the case of two metals with a ligand mixture (Cit+Succ), the calculation gives Δlog β = +1.8 (i.e., $E \approx 10^{-10} \approx 6^3$), indicating strong synergy when Cu and Zn are present together in the center of the mixture—a space organized by structural/distributive solutions that allow each metal to stabilize without intense direct competition [16]. Therefore, we can tentatively conclude that: (a) the simultaneous binding of two ligands to a single metal center usually leads to competition and resistance, while (b) the presence of two metals in their mixed ligand system may generate stable heterometric arrangements that increase the overall stability of the system. All calculations were performed according to equations (1,2,3) and as listed in Table (2).

Table 2. Integrated Δlogβ Synergism/Antagonism

System	**Logβ (mixed)**	**Σ logβ (individual)**	**Δlogβ**	**E = 10 $^{\Delta log\beta}$**	**Interpretation**
Cu (Cit+Succ)	11.7	15.8	-4.10	7.9×10^{-5}	Strong antagonism
Zn (Cit+Succ)	9.4	12.4	-3.00	1.0×10^{-3}	Antagonism
Cu+Zn on Succ	11.4	11.2	+0.20	1.6	Mild synergism
Cu+Zn on Cit	14.0	17.0	-3.00	1.0×10^{-3}	Strong antagonism
Cu+Zn with Cit+Succ	22.9	21.1	+1.80	≈63.1	Strong synergism

Ionic Distribution Curves

Figure (4) illustrates the distribution of protonation species (α_0–α_4) for the mixed citric–succinic acid system across the examined pH range. Each α-curve represents the mole fraction of a specific protonation state at equilibrium, reflecting the sequential deprotonation steps governed by the combined pKa values of the two acids. At low pH, the fully protonated species (α_0) predominates due to the high availability of hydrogen ions stabilizing all carboxyl and hydroxyl functional groups. As the pH increases, the partially deprotonated forms α_1 and α_2 emerge and reach their maxima at pH values close to the apparent pKa values of the corresponding deprotonation steps. The broadness and overlap of these curves highlight the cooperative behaviour of the mixed system, where the protonic equilibria of citric and succinic acids influence each other, giving rise to merged and shifted distribution profiles compared to individual acid systems.

In the intermediate pH region, co-existence of multiple α-species becomes evident, indicating that differently protonated ligating sites are simultaneously available. This has direct implications for metal–ligand coordination: citric acid contributes multiple carboxylates and a central hydroxyl donor, whereas succinic acid provides a linear dicarboxylate unit. The relative dominance of α_2 and α_3 in this region marks the pH window in which mixed chelation is most favourable, as both acids present partially deprotonated states capable of forming stable, multidentate interactions with metal ions. At higher pH values, the fully deprotonated species (α_4) becomes predominant, consistent with complete loss of acidic protons and the generation of highly anionic forms with increased electron-donating capacity.

Overall, the speciation diagram provides a mechanistic interpretation of how protonic equilibria shape the coordination environment in the mixed citric–succinic system. The progressive transitions between protonation states, together with the overlap of intermediate species, define the pH domains in which mixed-metal complexes are expected to form, stabilize, or undergo structural changes.

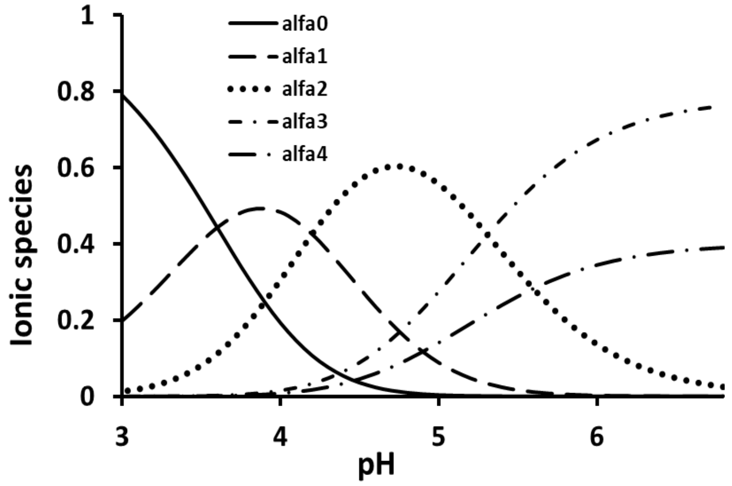

Figure 4. Ionic distribution curve of a mixture of citric and succinic acids

The distribution diagram for copper in the mixed citric–succinic acid system (Figure 5) shows the sequential formation of three distinct complexes—ML, ML_2, and ML_3—across the pH range 3–6. At low pH (≈3.0–3.5), the free copper ion (M) dominates, reaching its maximum abundance around 3.1×10^{-13}. As the pH increases, M decreases sharply and is progressively replaced by the monoligand complex ML, which becomes the predominant species between pH 3.6 and 4.4, with a clear maximum near pH ≈ 4.0 at approximately 3.0×10^{-13}. Further increase in pH leads to the rapid emergence of the biligand complex ML_2, which shows a broad and highly pronounced peak centered near pH 4.9–5.1, reaching around 4.0×10^{-13}, making ML_2 the dominant species within the mid-pH region of the diagram. At higher pH values (above ~5.2), the triligand species ML_3 begins to form and steadily increases in abundance. ML_3 becomes significant in the pH 5.5–6.2 range, reaching its highest level close to 1.7×10^{-13}, although it never surpasses ML_2 in dominance. This behaviour is consistent with the established understanding that, in polycarboxylate systems, the acid–base equilibria of the ligands themselves dominate the pH range at which complexation occurs, while the metal ion primarily influences the fractional abundance of each species rather than the shape of the distribution curves [22,23].

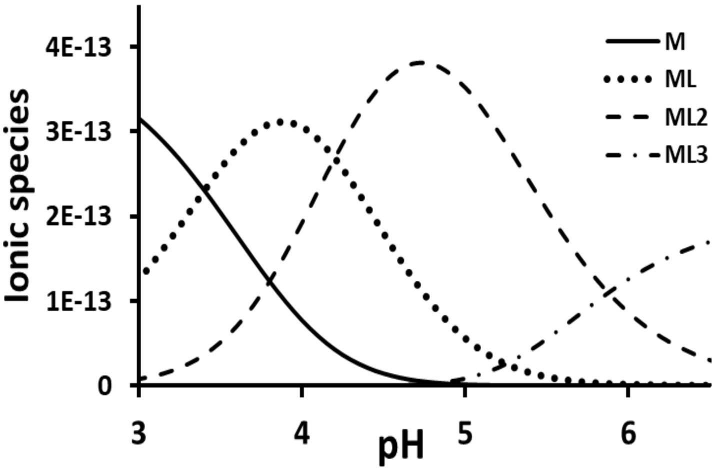

Figure 5. Ionic distribution curve of copper with a mixture of citric and succinic acids

The ionic-species distribution diagram of the Zn–Cit+Succ system (Figure 6) reveals a well-defined pH-dependent shift among the free metal ion (M), the 1:1 complex (ML), and the 1:2 complex (ML_2). At pH values below 3.5, the free Zn^{2+} species predominates, reflecting the extensive protonation of both citric and succinic acids, which suppresses ligand availability for coordination. As the pH increases toward 4.0–4.3, the concentration of ML rises sharply and reaches its maximum, indicating that partial deprotonation of the carboxylate groups creates the optimal window for the formation of the first coordination sphere. This behaviour is consistent with the moderate stability of the 1:1 complex ($\log \beta_1 = 5.4$), which becomes competitive only once ligand deprotonation becomes thermodynamically favorable. Beyond pH ≈ 4.8, the ML species gradually declines while the ML_2 species becomes dominant, reaching its maximum around pH 5.0–5.3. The transition toward ML_2 reflects the availability of additional deprotonated sites and agrees with the lower but still significant stability constant of the 1:2 complex ($\log \beta_2 = 4.0$). The overall pattern demonstrates that, under mixed-ligand conditions, Zn^{2+} undergoes a sequential and pH-controlled coordination pathway, where the predominance of ML_2 at mildly acidic to near-neutral pH highlights the enhanced binding capacity of the combined citric–succinic system once both ligands are sufficiently deprotonated.

This difference reflects the intrinsic disparity in the stability constants of the two metals: copper forms stronger complexes (higher log β values), resulting in lower calculated free-metal and bound-species fractions under identical total-metal and ligand conditions [24]. Conversely, zinc—despite forming weaker complexes—exhibits slightly higher calculated species fractions within the same ligand framework, a phenomenon commonly observed in mass-balance speciation modeling where ligand protonation equilibria constrain the overall pH-dependent behaviour [23]. These findings are fully aligned with classical and modern coordination-chemistry references showing that polyprotic, multidentate ligands such as citrate and succinate strongly dictate the pH window of speciation for divalent metals, causing different metals to produce similar distribution shapes, with the primary difference being the magnitude of the fraction curves rather than their position or width [22-24].

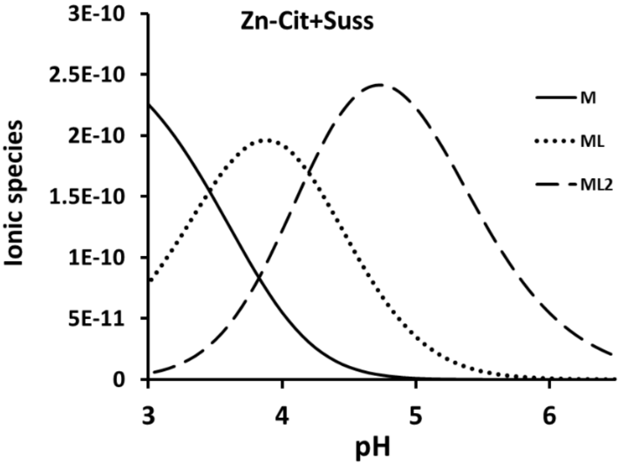

Figure 6. Ionic distribution curve of zinc with a mixture of citric and succinic acids.

The distribution diagram of the mixed-metal system Succ–Cit + Cu + Zn (Figure 7) presents a markedly different speciation pattern compared with the individual Cu and Zn-only systems. The mixed-metal profile displays broader and more overlapping curves, reflecting simultaneous competition between the two metal ions for the same ligand sites. The mixed-metal diagram reveals the formation of multiple polynuclear species (ML_2, ML_3, and ML_4) extending across a wide pH range. In this mixed system, the free metal concentration (M) decreases more gradually than in the Cu-only plot, as both Cu^{2+} and Zn^{2+} contribute to the collective M signal. The ML species reaches a maximum around pH 3.8–4.0, similar to the Zn-only system but at slightly higher concentrations; however, it is rapidly overtaken by ML_2, which becomes the dominant species between pH 4.5 and 5.2. The presence of ML_3 and ML_4, absent in the Zn-only and significantly less pronounced in the Cu-only system, indicates that the combined presence of Cu and Zn facilitates the stabilization of higher-order complexes. This stabilization likely arises from the cooperative effect of different coordination preferences of Cu^{2+} and Zn^{2+}, allowing the ligand to accommodate successive deprotonation and gradual metal binding as pH increases.

Compared with the Cu-only diagram, where peak heights lie within the 10^{-13} – 10^{-14} range, the mixed Cu+Zn system exhibits higher concentration levels on the vertical axis (10^{-11} range), more similar to the Zn-only behaviour. However, the emergence of ML_3 and ML_4 in the mixed system results in a much broader distribution envelope than seen in either single-metal system .

Overall, the mixed-metal speciation profile represents an intermediate yet more complex behaviour: broader than Cu-only, because the high stability of Cu complexes is modulated by the presence of Zn^{2+}; richer in higher-order species than Zn-only, due to Cu's strong binding assisting stepwise ligand coordination; and higher in absolute concentrations than Cu-only, reflecting the combined metal contribution and the stabilizing influence of Zn on intermediate species.

This highlights that the coexistence of Cu^{2+} and Zn^{2+} fundamentally alters both the shape and magnitude of the distribution curves, creating a speciation landscape that cannot be predicted from either metal in isolation.

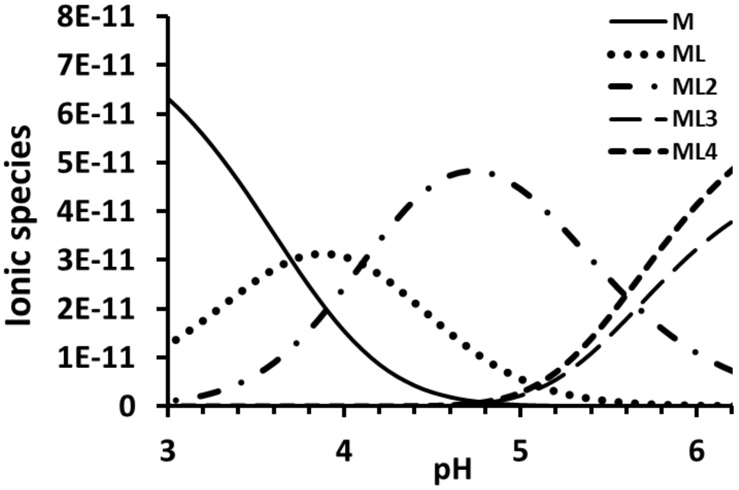

Figure 7. Ionic distribution curve of copper and zinc with a mixture of citric and succinic acids

Conclusion

The mixed citric–succinic ligand system exhibits a complex interplay of cooperative and antagonistic behaviours. While ternary complexes formed by a single metal with both ligands show clear antagonism particularly on citratethe full mixed-metal system (Cu^{2+} + Zn^{2+}) displays strong synergism, as reflected by the significantly positive $\Delta\log\beta$ (+1.8) and the high overall stability ($\log \beta = 22.9$). This enhancement arises from heterometallic arrangements in which succinate provides the more favourable coordination environment, whereas citrate contributes selectively without serving as a central binding framework. The results highlight that stability in multi-ligand systems is not dictated by acidity alone but emerges from complementary metal–ligand interactions that minimise competition and optimise spatial binding. These insights deepen our understanding of mixed-ligand, mixed-metal equilibria and may support the design of more effective chelating and separation systems.

Disclaimer

The article has not been previously presented or published, and is not part of a thesis project.

Conflict of Interest

There are no financial, personal, or professional conflicts of interest to declare.

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