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Mixed Metal Complexes of Succinic Acid: The Effect of pH and Ionic Speciation Modeling

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سلوك المعقّدات الفلزية المختلطة لحمض السكسنيك: تأثير تغيّر الأس الهيدروجيني ونمذجة الأنواع الأيونية

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Abstract:
The potentiometric behavior of succinic acid (H_2Succ) and its complexation with copper(II) and zinc(II) ions were systematically investigated to elucidate the influence of pH and ionic speciation in single and mixed-metal systems. Titrations were performed at 25 °C in 0.1 M KCl to determine the acid dissociation and complex formation constants. The dissociation constants of the free ligand were found to be $pKa_1 = 4.6$ and $pKa_2 = 5.2$. In the presence of Cu^{2+} and Zn^{2+} ions, significant shifts in the potentiometric curves confirmed the formation of stable complexes, with stability constants log β = 6.3 for Cu^{2+}–Succ and log β = 4.9 for Zn^{2+}–Succ systems. The mixed Cu^{2+} + Zn^{2+} system exhibited synergistic stabilization with an overall log β = 11.4, suggesting the formation of binuclear or bridging mixed-metal complexes. Ionic speciation modeling demonstrated that the predominant species distribution depends strongly on pH, with Cu-containing complexes dominating in mildly acidic to neutral conditions. These findings highlight the cooperative interactions between Cu^{2+} and Zn^{2+} in mixed systems and provide insight into the coordination chemistry of dicarboxylic acids under varying protonation equilibria.

Keywords: Succinic Acid Complexes, Mixed-Metal, Potentiometric, Ionic Speciation.

الملخص:
دُرست منهجية السلوك الجهدي لحمض السكسينيك (H_2Succ) وتكوينه مع أيونات النحاس (II) والزنك (II) لتوضيح تأثير الرقم الهيدروجيني والتكوين الأيوني في الأنظمة المعدنية المفردة والمختلطة. أُجريت معايرات عند درجة حرارة 25 درجة مئوية في 0.1 مولار كلوريد البوتاسيوم لتحديد ثوابت تفكك الحمض وتكوين المعقد. وُجد أن ثوابت تفكك الربيطة الحرة هي $pKa_1 = 4.6$ و $pKa_2 = 5.2$. بوجود أيونات Cu^{2+} و Zn^{2+}، أكدت التحولات الكبيرة في المنحنيات الجهدية تكوين معقدات مستقرة، بثوابت استقرار log β = 6.3 لأنظمة Cu^{2+}–Succ و log β = 4.9 لأنظمة Zn^{2+}–Succ. أظهر نظام Zn^{2+} + Cu^{2+} المختلط استقرارًا تآزريًا مع log β = 11.4 كليًا، مما يشير إلى تكوين معقدات معدنية مختلطة ثنائية النواة أو جسرية. أظهرت نمذجة الأنواع الأيونية أن توزيع الأنواع السائد يعتمد بشدة على الرقم الهيدروجيني، مع هيمنة المعقدات المحتوية على النحاس في الظروف الحمضية المعتدلة إلى المتعادلة. تسلط هذه النتائج الضوء على التفاعلات التعاونية بين Cu^{2+} و Zn^{2+} في الأنظمة المختلطة، وتوفر نظرة ثاقبة على كيمياء التنسيق للأحماض ثنائية الكربوكسيل في ظل توازنات بروتونية متفاوتة.

الكلمات المفتاحية: معقدات حمض السكسنيك، فلزات مختلطة، مقياس الجهد، الأنواع الأيونية.

Introduction:

Succinic acid (H_2Succ), a simple aliphatic dicarboxylic acid ($HOOC–CH_2–CH_2–COOH$), plays a significant role in coordination chemistry due to its two carboxylic groups that can act as bidentate or bridging ligands toward metal ions [1]. Through its ability to chelate and form hydrogen-bonded networks, succinic acid serves as a model system for understanding metal–ligand interactions in biological and synthetic environments [2].The coordination behavior of succinic acid with transition metals such as Cu(II), Zn(II), and Ni(II) has been widely studied because of their biological relevance and catalytic potential. These metal ions are essential in enzymatic processes, redox reactions, and structural stabilization in metalloproteins [3]. The ability of succinate to form complexes with such ions provides insight into metal–carboxylate binding modes that are central to biochemical systems and environmental metal transport [4].

Potentiometric titration is a well-established technique for determining acid dissociation constants (pKa) and metal–ligand stability constants (log β) in aqueous media. It offers a precise quantitative evaluation of equilibrium species and allows for constructing distribution diagrams that describe ionic speciation across a wide pH range [5,6]. In the case of dicarboxylic acids, potentiometry provides direct evidence of protonation equilibria and metal–ligand interactions through measurable pH shifts during titration.

Although the coordination chemistry of succinic acid with individual transition metals such as Cu(II), Zn(II), and Ni(II) has been reported [7-9], comparative and mixed-metal potentiometric studies remain limited. Most previous investigations have focused on isolated complexes or on solid-state characterization using spectroscopic or crystallographic methods [10,11], whereas solution-phase equilibrium data describing the interaction, competition, and cooperation between different metal ions are scarce. Moreover, mixed-metal systems involving Cu^{2+} and Zn^{2+} are of particular biochemical and catalytic interest because many metalloenzymes, such as superoxide dismutase, contain both Cu and Zn centers functioning cooperatively [3,4]. However, the ionic speciation behavior of such systems as a function of pH has not been quantitatively modeled for succinic acid, a biologically relevant dicarboxylate ligand.

Therefore, the present study aims to fill this gap by providing a precise potentiometric evaluation of succinic acid with Cu(II), Zn(II), and their combination under identical experimental conditions; constructing ionic speciation models to visualize the effect of pH on complex formation and stability; and comparing the corresponding stability constants to elucidate potential synergistic or antagonistic effects in mixed-metal environments. In this context, the study contributes new quantitative thermodynamic and speciation data for Cu–Zn–succinate systems. These findings are expected to enhance the understanding of mixed-metal coordination chemistry and to provide insight into protonation and complexation equilibria relevant to biological and catalytic systems.

Material and methods:

Materials and Reagents:

- **Chemicals:**

Succinic acid (analytical grade), Zinc(II) nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), Copper(II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$), 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 acid was prepared at a concentration of 0.1 M, Zn^{2+}, and Cu^{2+} 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)(ligand)
c= b+ metal ion (1.0×10^{-3}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.

- **Data Treatment:**

Protonation constants of succinic acid and **stability constants** of binary and ternary complexes were calculated initially by Irving and Rossotti equations [12], then by using **Hyperquad2008** software. Species distribution diagrams were generated using Hyperquad Simulation and Speciation **(HySS).** 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:

Potentiometric Study of Free Succinic Acid:

The potentiometric titration curve (Figure (1)) of succinic acid in 0.1 M KCl at 25 °C displayed two clear inflection points corresponding to the dissociation of its two carboxylic groups. The dissociation constants were determined as $pKa_1 = 4.6$ and $pKa_2 = 5.2$ as listed in table (1). These values indicate a moderate acidity and align well with literature data [10, 13].

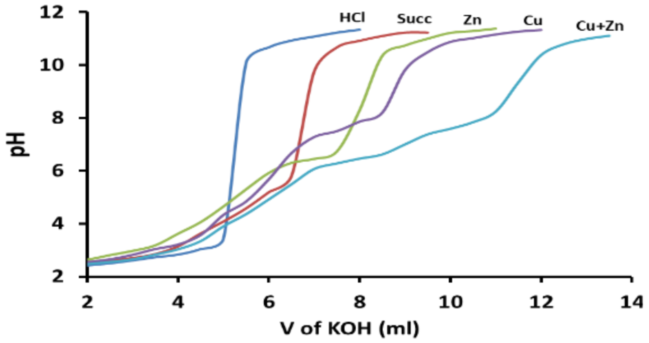

Figure (1): Potential titration curves of succinic acid with the metal ions of copper, zinc, and their mixture

Figure (2) illustrates the successive proton deposition transitions of succinic acid with increasing pH. The dissociation constants, $pKa_1 = 4.6$ and $pKa_2 = 5.2$, are within the known literature range (4.2–5.6) [14], confirming the accuracy of the experimental method and the stability of the ionic system used. The figure shows that the first transition from H_2Succ to $HSucc^-$ occurs gradually, while the second transition to $Succ^{2-}$ requires higher alkalinity, reflecting the effect of electrostatic repulsion between the increasing negative charges.

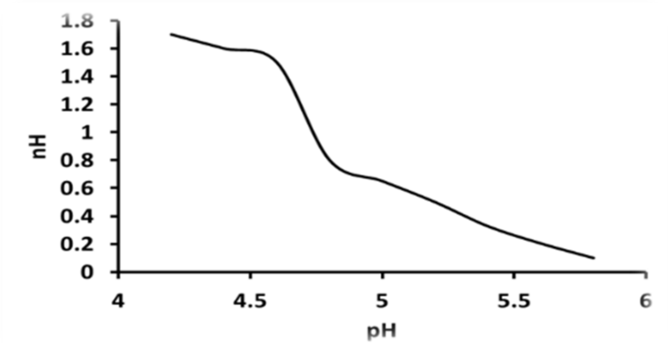

Figure (2): Proton dissociation curve of succinic acid

Metal Complex Formation:

Figure (3) displays the complex formation curves between succinic acid and copper and zinc ions, both individually and in combination. The increased slope of the curves upon the addition of Cu^{2+} indicates higher stability of the copper complexes compared to the zinc complexes. The combined curve (Cu + Zn) also exhibited intermediate behavior tending towards higher stability, suggesting metal-metal synergism that enhances the mutual affinity between the two ions on a single succinic acid molecule [15]. This synergism is often due to a redistribution of bonding sites, whereby each metal is bonded to a different carboxyl group within the same molecule, thus reducing repulsion and increasing overall stability.

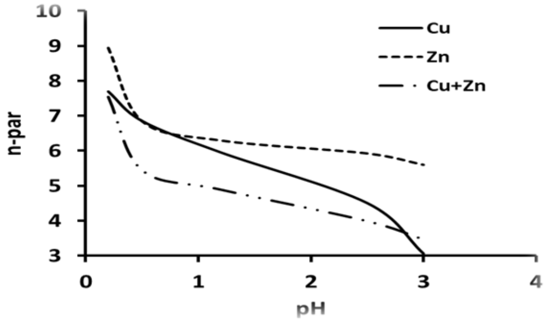

Figure (3): Formation metal complexes curves of copper and zinc ions and their mixture with succinic acid

Table (1): Dissociation and stability constants of succinic acid and its metal complexes

Ion / system	pKa1	pKa2	pKa3	pKa4	logKa1	logKa2	logβn
$Succ^{2-}$	4.6±0.1	5.2±0.2	—	—	—	—	—
Cu^{2+} - $Succ^{2-}$	—	—	—	—	6.3±0.12	—	6.3
Zn^{2+} - $Succ^{2-}$	—	—	—	—	4.9±0.09	—	4.9
Cu^{2+} + Zn^{2+} - $Succ^{2-}$	—	—	—	—	6.9±0.17	4.5±0.1	11.4

(±): standard deviation, n=(3)

Ionic Species Distribution Curves of Succinic Acid:

The figure (4) illustrations the distribution of ionic species (H_2Succ, $HSucc^-$, $Succ^{2-}$) versus pH. It is evident that protonated species dominate at pH < 4, while $Succ^{2-}$ predominates at pH > 6, with a clear overlap between $HSucc^-$ and $Succ^{2-}$ in the 4.5–5.5 range, which is consistent with experimental pKa values. This behavior indicates gradual and balanced transitions of proton dissociation, which enhances solution stability and reduces experimental distortions [16].

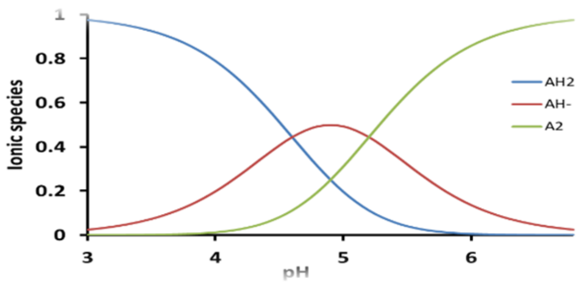

Figure (4): Ionic species equilibrium curve of succinic acid against pH.

Complexation with Cu(II) Ions:

In the presence of Cu^{2+} ions, the titration curve shifted to higher pH values compared to free acid, indicating complex formation (Figure (1). The calculated stability constant was log β = 6.3 (Table 1), suggesting moderate-to-high complex stability. The species distribution diagram showed [Cu(Succ)] as the dominant species around pH 5. The higher stability can be attributed to Cu^{2+}'s strong affinity for oxygen donors and its electronic structure that facilitates coordinate bonding. These findings agree with reported trends in dicarboxylic acid–Cu(II) systems [13].

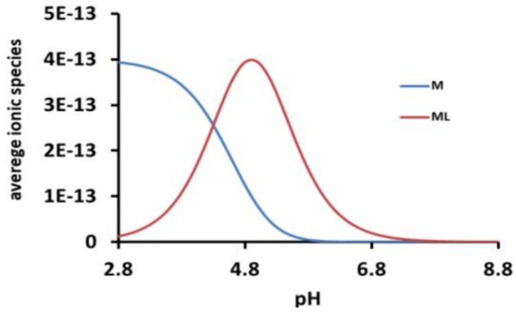

Figure (5): Ionic species equilibrium curve of Cu^{+2} with succinic acid against pH.

Complexation with Zn(II) Ions

The titration curve in the presence of Zn^{2+} exhibited a smaller pH shift, indicating weaker complex formation (Figure 1). The stability constant was determined as log β = 4.9 (Table 1). The species distribution diagram in Figure (6) showed [Zn(Succ)] forming in the pH range of 5–6, but in lower abundance than [Cu(Succ)]. The reduced stability is consistent with Zn^{2+}'s filled d^{10} configuration, which limits its ability to form strong coordinate bonds. This result aligns with literature reports where Zn^{2+} complexes exhibit lower stability constants than Cu^{2+} complexes [13].

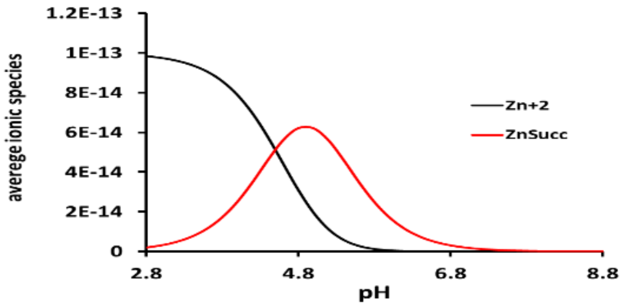

Figure (6): Ionic species equilibrium curve of Zn^{+2} with succinic acid against pH.

Mixed-Metal (Cu(II) + Zn(II)) System:

In the mixed-metal system, the titration curve (Figure 1) exhibited an overall greater pH shift and enhanced buffering capacity, indicating synergistic effects between Cu^{2+} and Zn^{2+}. The calculated formation constants were log K_1 = 6.9 and log K_2 = 4.5, yielding an overall log β = 11.4 (Table 1). The distribution diagram in Figure (7) suggested the formation of mixed complexes such as $[CuZn(Succ)_2]$, which remain stable in the pH range of 5.5–6.5. The enhanced stability arises from cooperative metal–ligand interactions, where Cu^{2+} contributes stronger coordination and Zn^{2+} stabilizes the overall structure. Such binuclear systems are of interest in catalysis and biomimetic chemistry due to their similarity to enzyme active sites.

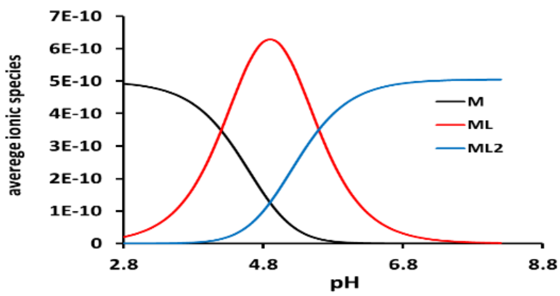

Figure (7): The ionic distribution diagram of mixed-metals complexes (Cu^{+2}+Zn^{+2}) of succinic acid

Conclusion:

The potentiometric analysis revealed that succinic acid exhibits two dissociation constants (pKa_1 = 4.6, pKa_2 = 5.2). Complexation with Cu^{2+} resulted in a more stable complex (log β = 6.3) compared to Zn^{2+} (log β = 4.9). The mixed-metal system displayed synergistic stability (log β = 11.4), suggesting the formation of binuclear complexes. The results confirm that Cu^{2+} has a higher coordination tendency than Zn^{2+} and that combined systems can yield more stable structures, consistent with coordination chemistry principles.

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