Studies on the Complexation of Succinic Hydrazide with Copper Chloride Salt

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ABSTRACT

The electrochemical behavior of the complexation between copper chloride salt and succinic hydrazide can be explained using cyclic voltammetric measurements. The complex is formed through the interaction with nitrogen and hydroxyl group or carbonyl group of succinic hydrazides. This interaction can be observed by decreasing in the height peak of current and measuring the (anodic/cathodic) shift of the potentials. All the solvation and thermodynamic parameters for the interaction of copper ions with succinic hydrazide as stability constant, Gibbs free energies, enthalpies and entropies of interaction were calculated. Finally, the activity of the formed complex was compared with the succinic hydrazide by comparing their effects on different types of gram-negative bacteria and fungi indicating high activity of the formed complex and its ability to be used in different medical applications.

Keywords: Succinic hydrazide, Complexation, Cyclic voltammetry, Solvation and Kinetic parameters, Stability constant, Antimicrobial activity.

I. INTRODUCTION

Electroanalytical techniques have been found a wide application in the characterization of the formed complex in a solution. Cyclic voltammetry is the first experiment performed in an electrochemical study of a compound, biological material or an electrode surface due to its capability for rapidly observing the redox behavior over a wide potential range [1-3].

Organic chemists used this technique to study the electrochemically generated free radicals while inorganic chemists used it to evaluate the effects of ligands on the oxidation and reduction potential of the central metal ion in complexes. This information can be useful for nonanalytical purposes as the studies of the oxidation and reduction process, adsorption process in various media and electron transfer processes at chemically modified electron surfaces [4-7].

In our work, we use the cyclic voltammetry to study the interaction between copper ions and succinic hydrazide in 0.1 M HCl using solid glassy carbon electrode and scan rate 0.1 V/Sec. The complex formation was observed by the change in peak heights and shift in the anodic and cathodic couples of peaks of multivalent copper ions.

II. EXPERIMENTAL

A. Materials and Solvents

Copper chloride salt (CuCl₂.2H₂O) with Mol.Wt equal 170.48 g/mol, Succinic hydrazide as a ligand and ethanol (EtOH) as analytical reagent grade material were used in this study and all from Merck Company. Hydrochloric acid pure (HCl) from Advic Co. and bidestilled water was prepared in our laboratory with conductivity of 3 μS cm⁻¹.

B. Preparation of Copper Complex

A traditional method was used to prepare the copper complex by refluxing 1 mmol of CuCl₂.2H₂O salt under investigation with 1 mmol of Succinic hydrazide using an ethanolic solution for 2-3 h close to the boiling point of the solvent. Then, the precipitate was filtered off, washed...
several times with absolute ethanol and dried in vacuum desiccators over anhydrous calcium chloride. Finally, the complex was characterized by using different techniques.

C. Cyclic Voltammetry

The cyclic voltametric studies were done by using DY2000 multichannel potentiometer, delivered from USA. It was connected to a cell of three electrodes; silver/silver chloride put in saturated KCl solution used as reference electrode, solid glassy Carbon electrode (SGC) was used as working electrode and platinum wire as auxiliary electrode. The solid glassy Carbon electrode (SGR) surface was polished to mirror state using (1-0.03) µ alumina powder. The SGR was washed with absolute alcohol and doubly distilled water till removing any adhering alumina particles. Area of electrode is (7.068x10⁻²) cm². The system was applied from (1 to -1) V potential window and (0.1, 0.02, 0.01) V.s⁻¹ scan rates. Passing purified N₂ was done before each experiment to insure inert atmosphere and diffusion experiment. Finally, the data was analyzed using origin software.

D. Biological Activity (Antibacterial and Antifungal) Activity

The antimicrobial activities of Succinic hydrazide and its complex were studied on LB agar by the disc diffusion technique against clinical isolates of gram-negative bacteria (Enterobacter, Staphylococcus aureus) and Fungi (Candida albicans).

Sterile filter paper discs (6mm) were individually immersed in Dimethylsulfoxide (DMSO) extract of Succinic hydrazide, copper complex and DMSO was taken as control. All the discs were dried, placed on the surface of the test bacterial and fungal and incubated for 18 to 24 h at 37 °C. The standard antibiotic used is Ceftazidime (30 µg) and finally the size of inhibition zones was measured.

III. RESULTS AND DISCUSSION

A. Infrared Analysis (IR)

Infrared spectra (IR) are an important and popular tool for structural elucidation and compound identification. IR of Succinic hydrazide and its complex with copper chloride salt were obtained by detecting changes in transmittance (or absorption) intensity as a function of frequency (Fig. 1, 2).

From IR spectra of Succinic hydrazide two symm (-NH) group appear at wavenumber (3312 and 3287) cm⁻¹, respectively. Also, two amidic (C=O) appear at wavenumber (1627 and 1608) cm⁻¹, respectively and (N-H) bend appear at 1532 cm⁻¹ (Fig. 1).

In IR spectra of copper complex indicates presence of a broad band at 3481 cm⁻¹ due to water molecules, the two symm (-NH) group shifted to lower wavenumber (3234 and 3137) cm⁻¹, respectively. One amidic (C=O) shifted to higher wavenumber 1635 cm⁻¹ while the other amidic (C=O) shifted to lower wavenumber 1579 cm⁻¹ and the (N-H) bend appear at 1542 cm⁻¹ (Fig. 2). This indicates the formation of complex between CuCl₂ salt and Succinic hydrazide.

B. Cyclic Voltammetry (CV)

1. Solvation and kinetic parameters in absence of Succinic hydrazide

The redox behavior of Cu²⁺ ions was examined in 30 ml HCl (0.1) M as a supporting electrolyte from (1 to -1) V of potential window and the measured current unit is Ampere, whereas the scan is 0.1 V/S (volt per second) at 290.65 K (Fig. 3). The copper chloride solution is added step wisely from 0.5 ml (1.64 x 10⁻³) M to reach 1.6 ml (5.06 x 10⁻³) M (Fig. 4).

The electrochemical redox behavior of Cu²⁺ ions at the solid glassy carbon electrode was studied at the steady state current, cyclic waves were obtained and explained using the following equations [8-18]:

\[ i_p = 0.4463 \, n \, F \, A \, C \, (n \, F \, D \, v/ \, R \, T)^{1/2} \]  
\[ \Delta E_p = E_{pR} - E_{pC} \]  
\[ k_p = 2.18* \left[ D_C \, \alpha \, n_a \, F \, v/RT \right]^{0.5} \exp \left[ \alpha^2 nF \, \Delta E_p/RT \right] \]  
\[ \alpha n_a = 1.857 \, RT \, / \, (E_{pC} - E_{pR/2}) \, F \]  
\[ \Gamma = i_p \, 4RT \, n^2 \, F^2 \, A \, v \]  
\[ Q = n \, FA \, \Gamma \]

where, \( i_p \) is the current in Ampere , A is the surface area of working electrode in cm² , D is the diffusion coefficient in cm²/Sec, v is the scan rate in volts/Sec, C is the
concentration of the Cu²⁺ ions, ΔEₚ is the peak potential difference, n is the number of electrons in redox reactions, kᵣ is the standard heterogeneous electron transfer rate constant in cm/sec, α is charge transfer coefficient, nₑ is the number of electron transfer in the rate determining step, Eₚ/ᵣ is the half wave potential for cathodic peak, Γ is the surface coverage in mol.cm⁻² and Q is the quantity of charge consumed during the reduction or adsorption of the adsorbed layer.

Fig. 3. Cyclic voltammogram of 30 ml HCl (0.1) M and scan rate 0.1 V/S at 290.65K.

Table I (A): The Solvation and Kinetic Parameters [Eₚ, Eᵣ, Iₚ, ΔEₚ, Eᵣ] of Different Cu²⁺ Ions Concentrations at Scan Rate 0.1 V/S and 290.65 K.

| ml of M | [M] x10⁻³ (mol L⁻¹) | Eₚ (V) | Eᵣ (V) | (-)Iₚ x10⁻³ (A) | Iₚ x10⁻⁴ (A) | ΔEₚ (V) | Eᵣ (V) |
|--------|------------------|-------|-------|----------------|-------------|--------|-------|
| 0.5    | 1.64             | 0.0044| 0.2633| 0.678          | 2.16        | 0.259  | 0.239 |
| 0.7    | 2.28             | 0.022 | 0.2356| 1.10           | 3.49        | 0.2136 | 0.2166 |
| 0.9    | 2.91             | 0.0411| 0.2276| 1.75           | 5.34        | 0.1865 | 0.2012 |
| 1.1    | 3.54             | 0.0487| 0.2185| 2.26           | 6.17        | 0.1698 | 0.197 |
| 1.3    | 4.15             | 0.0518| 0.2176| 2.78           | 7.36        | 0.1638 | 0.1885 |
| 1.4    | 4.46             | 0.0512| 0.2118| 3.09           | 7.61        | 0.1606 | 0.1868 |
| 1.6    | 5.06             | 0.0553| 0.2084| 3.57           | 9.47        | 0.1532 | 0.1841 |

Table I (B): The Solvation and Kinetic Parameters [Dₚ, Dᵣ, kᵣ, Γ, Γₛ, Q, Qₛ] of Different Cu²⁺ Ions Concentrations at Scan Rate 0.1 V/S and 290.65 K.

| ml of M | [M] x10⁻³ (mol L⁻¹) | Dₚ (cm².s⁻¹) | Dᵣ (cm².s⁻¹) | kᵣ (mol.cm⁻².s⁻¹) | Γ (mol/cm²) | Γₛ (mol/cm²) | (+)Qₛ | (+)Qₛ | x10⁶(C) |
|--------|------------------|-------------|-------------|-----------------|-------------|-------------|--------|--------|--------|
| 0.5    | 1.639           | 0.5938      | 5.8450     | 0.0823          | 2.5237      | 0.7917     | 0.34425| 1.0800 |
| 0.7    | 2.2801          | 0.7840      | 7.9372     | 0.0432          | 4.0332      | 1.2832     | 0.55014| 1.7504 |
| 0.9    | 2.9126          | 1.2195      | 11.364     | 0.0255          | 6.4253      | 1.9614     | 0.87644| 2.6755 |
| 1.1    | 3.5370          | 1.3807      | 10.270     | 0.0193          | 8.3026      | 2.2643     | 1.1325 | 3.0886 |
| 1.3    | 4.1534          | 1.5113      | 10.610     | 0.0155          | 10.2003     | 2.7026     | 1.3914 | 3.6865 |
| 1.4    | 4.4586          | 1.6268      | 9.8367     | 0.0145          | 11.3604     | 2.7935     | 1.5946 | 3.8105 |
| 1.6    | 5.0633          | 1.6801      | 11.812     | 0.0139          | 13.1111     | 3.4764     | 1.7884 | 4.7419 |

Fig. 5 gives straight lines from the relation between cathodic and anodic peak current Iₚ against different concentrations of Cu²⁺ ions in 0.1M HCl, indicating diffusion process.

Two couples of copper ion peaks were obtained the first two cathodic peaks on the scan towards negative potentials and the second at reversal of scan shows two well defined anodic peaks (see Fig. 4). The cathodic couple of peaks are attributed to the reduction of Cu²⁺ to Cu⁺ and then to Cu as cathodic mechanism. Then Cu transfers to Cu⁺ and Cu²⁺ as anodic mechanism. Fig. 4 gave the effect of scan rate on the peak potential and peak current.

Fig. 5: The relation between peak current Ip (Ipa - Ipc) against different Cu⁺ ions concentration at 290.65 K and scan rate 0.1 V/S.
1.2. Effect of different scan rates

Effect of different scan rates for the redox behavior of Cu²⁺ ions in 0.1 M HCl was studied at (0.1, 0.02, 0.01) (V.s⁻¹) and 290.65 K (Fig. 6). The solvation and kinetic parameters (Ep, Ip, ΔEp, Ep, D, kₜ, Δ and Q) of different scan rates of Cu²⁺ ions were presented in Table II (A, B).

The cathodic mechanism showed nearly constant peak current from the relation with square root of scan rate indicating it is diffusion controlled process while the anodic mechanism of dissolution of the deposited copper at the cathodic potential is a stripping process.

![Fig. 6. Cyclic voltammogram of different scan rates of (5.06×10⁻⁴) M Cu²⁺ ions in 0.1 M HCl at 290.65K.](image)

![Fig. 7. The relation between peak current Ip (Ipc - Ipₐ) against the square root of different scan rates for (0.1) M Cu²⁺ ions at 290.65 K.](image)

2. Solvation and kinetic parameters in presence of Succinic hydrazide

2.1. Effect of different copper ions concentrations in presence of Succinic hydrazide

The electrochemical redox behavior of Cu²⁺ ions in the presence of Succinic hydrazide at the solid glassy carbon electrode was studied at the steady state current and cyclic waves were explained using equations (1-6) (Fig. 8). The solvation and kinetic parameters (Ep, Ip, ΔEp, Ep, D, kₜ, Δ and Q) of interaction of (5.06×10⁻⁴) M Cu²⁺ ions and different concentrations of Cu²⁺ ions at 290.65 K and scan rate 0.1 V/S were presented in Table III (A, B).

![Fig. 8. The relation between peak current Ip (Ipc - Ipₐ) against the square root of different scan rates for (0.1) M Cu²⁺ ions at 290.65 K.](image)

2.2. Effect of different scan rates

Effect of scan rate on the interaction between Cu²⁺ ions and Succinic hydrazide was studied in (0.1, 0.02 and 0.01) V.S⁻¹ (Fig. 10). The solvation and kinetic parameters (Ep, Ip, ΔEp, Ep, D, kₜ, Δ and Q) of different scan rates of Cu²⁺ ions in the presence of Succinic hydrazide were presented in Table VI (A, B).

![Fig. 10. The relation between peak current Ip (Ipc - Ipₐ) against the square root of different scan rates for (0.1) M Cu²⁺ ions at 290.65 K.](image)
TABLE III (B): THE SOLVATION AND KINETIC PARAMETERS (D, D, k, Γ, Q, Q) OF INTERACTION OF (5.06x10^-3) M Cu^{2+} IONS AND DIFFERENT CONCENTRATIONS OF Succinic hydrazide at 290.65 K AND SCAN RATE 0.1 V/S

| [M] x10^-3 | [L] x10^{-3} | k x10^4 | Γ_a x10^4 | Γ_c x10^4 | (-)Q_a x10^{-5} | (+)Q_c x10^{-5} |
|------------|--------------|----------|------------|------------|-----------------|-----------------|
| 4.984      | 0.6307       | 15.90    | 16.42      | 0.0131     | 12.55           | 4.035           |
| 4.954      | 0.8775       | 13.88    | 14.85      | 0.0126     | 11.66           | 3.814           |
| 4.923      | 1.121        | 12.14    | 13.82      | 0.0117     | 10.83           | 3.657           |
| 4.893      | 1.362        | 10.95    | 12.48      | 0.0109     | 10.23           | 3.453           |
| 4.863      | 1.600        | 9.987    | 7.358      | 0.0091     | 9.709           | 2.635           |
| 4.848      | 1.786        | 9.763    | 8.202      | 0.0104     | 9.570           | 2.774           |
| 4.819      | 1.951        | 8.016    | 8.079      | 0.0112     | 8.620           | 2.736           |
| 4.420      | 5.145        | 8.039    | 3.423      | 0.0089     | 7.917           | 1.634           |
| 4.082      | 7.850        | 6.706    | 3.532      | 0.015      | 6.677           | 1.532           |

TABLE IV (A): THE SOLVATION AND KINETIC PARAMETERS (Ep, Ep, Ip, Ip, ∆Ep, ∆Ep) OF DIFFERENT SCAN RATES OF COPPER COMPLEX AT 290.65K

| D (v) | [M] x10^-3 (mol. L^-1) | [L] x10^{-3} (mol. L^-1) | Ep (v) | ∆Ep (v) | Ip (A) x10^{-5} | ∆Ep (v) |
|-------|------------------------|--------------------------|--------|---------|----------------|---------|
| 0.1   | 4.082                  | 7.850                    | 0.0528 | 0.2281  | 1.8183         | 7.154   |
| 0.02  | 4.082                  | 7.850                    | 0.0486 | 0.2042  | 1.0199         | 3.104   |
| 0.01  | 4.082                  | 7.850                    | 0.0555 | 0.1942  | 0.8749         | 2.442   |

TABLE IV (B): THE SOLVATION AND KINETIC PARAMETERS (D, D, k, Γ, Q, Q) OF DIFFERENT SCAN RATES OF COPPER COMPLEX AT 290.65K

| D (v) | [M] x10^-3 (mol. L^-1) | [L] x10^{-3} (mol. L^-1) | k x10^4 | Γ_a x10^4 | Γ_c x10^4 | (-)Q_a x10^{-5} | (+)Q_c x10^{-5} |
|-------|------------------------|--------------------------|----------|------------|------------|-----------------|-----------------|
| 0.1   | 4.082                  | 7.850                    | 0.6706   | 1.038      | 0.2574     | 0.677           | 2.627           |
| 0.02  | 4.082                  | 7.850                    | 1.055    | 0.9772     | 8.651      | 1.873           | 5.700           |
| 0.01  | 4.082                  | 7.850                    | 1.553    | 1.209      | 4.916      | 3.213           | 8.966           |

Fig. 8. Cyclic voltammograms for the interaction of (5.06x10^-3) M Cu^{2+} ions with different concentrations of Succinic hydrazide at 290.65K and scan rate 0.1 V/S.

Fig. 9. The relation between peak current Ip (Ip, Ip) against different Cu^{2+} ions concentration in the presence of Succinic hydrazide at 290.65 K and scan rate 0.1 V/S.

Fig. 10. Cyclic voltammogram of different scan rate of (4.08x10^-3) M Cu^{2+} ions with (7.85x10^-3) M Succinic hydrazide at 290.65K.

Fig. 11. The relation between peak current Ip (Ip, Ip) against different scan rates of copper complex at 290.65 K.
3. Electrochemical behavior of the complexation between Cu2+ ions and Succinic hydrazide

A stability constant is a measure of the strength of the interaction between the reagents that come together to form the complex.

The stability constants (βj) for copper complex for each addition are calculated by applying the following equations [19-28].

\[
\Delta E^* = E^*_{c} - E^*_{M} = 2.303 \text{ (RT/nF)} \ast (\log \beta_{j} + j \log C_{x}) \quad (7)
\]

\[
E^* = (E_{pa} + E_{pc})/2 \quad (8)
\]

\[
\Delta G = -2.303 \text{ RT log} \beta_{MX} \quad (9)
\]

where, \(E^*_{M}\) is the formal peak potential of metal at finally adding in the absence of Succinic hydrazide, \(E^*_{c}\) is the formal peak potential of metal complex after each addition.

4. Biological activity (Antimicrobial and Antifungal) activity

The antimicrobial activity was estimated based on inhibition zone size formed around discs of Succinic hydrazide and its complex on a petri dish with Luria Bertani agar (LB-agar) plates to measure the efficacy of the used compounds [29-34].

4.1. Antibacterial activity

The antibacterial activity of copper complex was compared with the activity of Succinic hydrazide using Enterobacter and Staphylococcus aureus (gram-negative bacteria) (Table VI). Presence of higher inhibition zone was observed around disc of copper complex with (9, 11) mm, respectively while absence of it around disc of Succinic hydrazide. So, it can act as bacteriostatic agent towards these bacteria (Fig. 13).

Table VI: Inhibition zone disc (mm) of Succinic hydrazide and copper complex with gram-negative bacteria and Fungi.

| Solid        | Inhibition zone disc (mm) | Type of gram-negative bacteria | Type of Fungi |
|--------------|---------------------------|--------------------------------|---------------|
| Succinic hydrazide | Absence  | Absence | Absence |
| Copper complex     | 9        | 11      | 7      |

4.2. Antifungal activity

Also, the experimental antifungal activity of copper complex was compared with the activity of Succinic hydrazide using Candida albicans (Table VI) indicating formation of higher inhibition zone (7 mm) around disc of copper complex only so, it can be used as antifungal drug (Fig. 14).

Fig. 12. The relation between Gibbs free energy (ΔG) against stability constant (β_{max}) at 290.65 K and scan rate 0.1 V/S.

Fig. 13. Inhibition zone discs (6mm) of [(1) Succinic hydrazide (2) copper complex] on the surface of an LB-agar plate with (a) Enterobacter (b) Staphylococcus aureus.
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