

Spectrophotometric, Potentiometric and Conductometric Study for Binary and Ternary Complexes of Fe (II) as Modeling of Fe-Polyphenol Prevention

Aisha A. Al-Abbassi¹, Matali Hassn¹, Aisha Maimoon¹, Khadija A. Ahmida¹, Noria Belkhar¹, Adel M. Najar^{2*}

¹Department of Chemistry, Sebha University, Elmarj, Libya; ²Department of Chemistry, Benghazi University, Elmarj, Libya

ABSTRACT

Stability constants of two and three complexes resulting from interactions of Fe(II) with Catechol (CAT) and Ascorbic Acid (AA) at equilibrium, were studied spectrophotometrically, potentiometrically and conductometrically. However, ferrous binary complex of vitamin C more stable than Fe(II) binary complex of catechol as stability constant revealed. The log K_2 values of CAT and AA/Fe(II) complexes recorded at 11.588 and 8.899 respectively. In ternary system; the stoichiometric ratio between M:L(AA):L(CAT) kept constant at 1:1:1. Experimentally; the $\Delta \log K$ coefficients were calculated; the positive values indicated that the ternary complexes is more stable than the binary complexes. However, addition of AA and Black tea to Fe (II) reported that disappear of d-d transition which indicate that the Fe-polyphenols complexes were not formed. Theoretically, molecular geometry and electronic structure of the molecules were calculated and discussed using DFT.

Keywords: Spectrophotometric; Catechol; Tea; Potentiometric; Polyphenols; Vitamin-C

INTRODUCTION

Vitamins and mineral deficiency directly affects humans all over the world and causes serious health problem globally [1] such as anemia which caused by chronic blood loss or malabsorption from food [2]. Moreover, consuming foods or drinks that contains substances impair iron absorption may causes this problem [3,4]. However, tea drink as one of the polyphenols substance that form Fe(III)-polyphenol complexes reported reduce the bioavailability of iron and make it unabsorbable [5,6].

Recently, using reducing agents such as Ascorbic acid (AA) may enhance the iron complexes absorption [7,8]. The main roles of AA for non-Heme dietary iron absorption: (i) prevent formation of insoluble Fe(III) complexes; (ii) reducing Fe(III) to Fe(II); which is preferred complexes for iron absorption in cells [9]. Although the iron and polyphenols reactions pH dependent and could not occur at low pH. Thus, using AA plays an important role to control pH of formed Fe(II) complex to be able to absorb into the body [7]. Additionally, using ferrous sulfate and AA at a

molecular ratio of 1: 0.6 respectively could effect and improve iron absorption of foods as well [10,11].

In this paper we have been used CAT and AA as polyphenols which reacted with Fe(II) to build binary and ternary systems using black tea. The tracking of binary and ternary systems absorbance have been studied spectrophotometrically, potentiometrically, conductometrically and theoretically.

EXPERIMENTAL MATERIALS

Materials

All chemicals utilized in this investigation were of the Analytical Reagent grade (AR) quality and the highest purity. L-Ascorbic acid (Labkem, >99%), Catechol (Philip Harris, $\geq 99.99\%$), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Carlo Erba, 98.8%), Sodium Hydroxide (Shandong, 98.8%), Hydrochloride acid (Scharlau Chemise, 36%) and black tea (sultan black tea-Srilanka).

Correspondence to: Adel M. Najar, Department of Chemistry, Benghazi University, Elmarj, Libya, Tel: 00218922623883; Email: Adle.njar@uob.edu.ly

Received: 04-Jul-2022, Manuscript No. MSO-21-001-PreQc-22; **Editor assigned:** 07-Jul-2022, PreQC No. MSO-21-001-PreQc-22 (PQ); **Reviewed:** 21-Jul-2022, QC No. MSO-21-001-PreQc-22; **Revised:** 24-Nov-2022, Manuscript No. MSO-21-001-PreQc-22 (PQ); **Published:** 02-Dec-2022, DOI: 10.35248/2469-9861.22.8.167

Citation: Al-Abbassi AA, Hassn M, Maimoon A, Ahmida KA, Belkhar N, Najar AM(2022) Spectrophotometric, Potentiometric and Conductometric Study for Binary and Ternary Complexes of Fe (II) as Modeling of Fe-Polyphenol Prevention. J Mass Spectrom Purif Tech. 8:167

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Solutions

Hydrochloric acid stock solution was prepared and titrated against standardized sodium hydroxide. The stock solution of AA (0.01M) was freshly prepared. A carbonate-free sodium hydroxide solution was prepared and standardized against standard oxalic acid solution before starting an experiment. The stock solution of ferrous chloride (0.01M) was prepared by dissolving the required quantities (0.199 g) in 100 mL deionized water and standardized by EDTA titrations. The stock solution of CAT (0.01M) prepared by dissolving the required quantities (0.110 g) in 100 mL deionized water.

Apparatus

Potentiometric titration performed by using a pH-meter model (Thermoelectric Corporation/Orion3 Star (pH Benchtop)(accuracy ± 0.002) with a glass and calomel electrodes assembly. The pH-meter was standardized before each titration with a buffer solution of pH=4.01, 7.00 and 10. The temperature

maintained constant (± 0.1) by a Grant Instruments (Cambridge) Ltd/SUB28 Thermostat Water Bath Apparatus. Conductometric titration and conductometric measurements were carried out by pH-conductivity meter Benchtop with an accuracy of ± 0.002 and a cell constant equal to 1 cm^{-1} . The Conductivity meter was standardized before each titration with a buffer solution of NaCl=1413 $\mu\text{S}/\text{cm}$ and 12.9 $\mu\text{S}/\text{cm}$. The reading recorded only when the instrument registered a steady value for at least one minute. Spectrophotometric measurements were recorded on a UV/Visible spectrophotometer with a spectral width of 2 nm, wavelength accuracy of 0.5 nm and a pair of 10 mm matched quartz cell is used to measure the absorbance of all the solutions, the spectral range of the instrument is from 200 nm to 900 nm.

Procedure

The experimental procedure involved the potentiometric titration of the following sets of solutions (Table 1):

*Titration	Components
HCl	(A)
CAT	(A) + (B)
AA	(A) + (C)
Binary complex(Cat)	(A) + (B)+ (D)
Binary complex(AA)	(A) + (C)+ (D)
Ternary complex	(A) + (B)+ (C) + (D)

Table 1: (A): The total volume used in each cell was 50 mL at $310.15 \pm 0.1 \text{ K}$. of HCl (0.1M, 10 mL); (B): Catechol (0.01 M, 10 mL); (C): Ascorbic acid (0.01 M, 10 mL); (D): Ferrous ion (0.01 M, 10 mL)] with a standardized 0.10 M NaOH solution.

Conductometric measurements

Conductometric measurements were carried out at 310.15 K by titration 50 mL of 0.01M of Fe^{2+} with 0.001M of AA and with 0.01M of CAT solution in 1 mL increments. Correction for the dilution effect is performed by multiplying the values of specific conductance by a factor $(50+v)/50$; where V is the volume of titrating added. The solution conductivity has been measured during the potentiometric titrations.

Black tea experiment

Preparation of black tea solution; 4 g of black tea was soaked in 200 mL of boiling water for 10 min and filtered. The filtrate had a concentration of 50 mg dried black tea/mL. In 4 conical flasks; a 10 mL of tea extract was placed; then 10 mL of ferrous chloride solution (0.001 M) were added to first flask, 10 mL of AA (0.001 M) in second flask, a mixture of (10 mL) AA and 10 mL of ferrous chloride solution in third flask. The fourth flask contained only tea extract. The flasks were placed in the shaker for period of 30 min, after which the absorption spectrum was recorded.

Computational details

Molecular geometry, HOMO/LUMO orbitals, and electronic structure of the ternary complex were calculated at the DFT level with DMol3 using the Materials Studio suite of programs (version 5.5). Structure optimization performed using a generalized gradient approximation (GGA) function [12,13] and a hybrid exchange-correlation function BLYP [14,15] with a Double Numeric plus Polarization (DNP) basis set to map the orbital structure of the compound.

RESULTS AND DISCUSSION

The interactions of ferrous ions with AA and CAT to form binary complexes and mixed ternary complexes were studied using potentiometric, conductometric and UV-spectroscopic methods. In addition, the binary and ternary complexes were undergone to (DFT) calculation to determine the HOMO/LUMO gap. In the potentiometric method, the ionization constant of AA and CAT and formation constants of the formed complexes have been tabulated at $37 \pm 1.0 \text{ }^\circ\text{C}$ (Figure

1).The proton-ligand dissociation constant equation (1) can be expressed as follow:

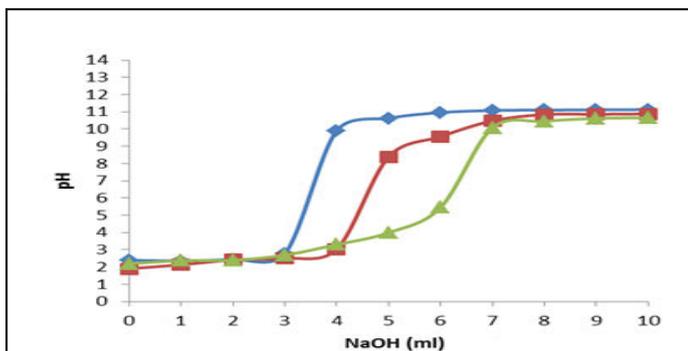


Figure 1: Potentiometric titration of AA and CAT at $37.0 \pm 0.1^\circ\text{C}$: (a) 0.1M HCl, (b) a +0.001M CAT,(c) a + 0.001M AA.

Note: (\blacklozenge) HCl, (\blacksquare) HCl+Cat,(\blacktriangle) HCl+AA.

The average number of proton attached per ligand was calculated at different pH values using Irving and Rossotti [16]. The value of proton-ligand dissociation constant for AA and CAT were obtained by plotting against pH (Figure 2).

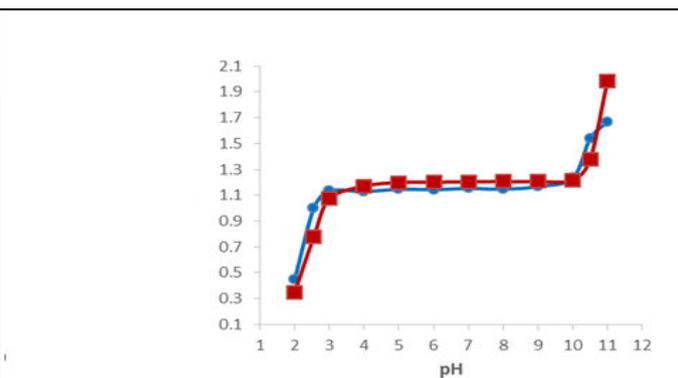


Figure 2: Potentiometric constant curve of ligands at $37.0 \pm 0.1^\circ\text{C}$: (a) CAT and (b) AA.

Note: (\blacklozenge)Catechol, (\blacksquare)AA, (\blacklozenge) HCl, (\blacksquare) HCl+Cat, (\blacktriangle) HCl+AA.

Binary complexes

Three types of titration were used to study the binary complexes: (a) free HCl; (b) (AA) with ferrous ions and (c) CAT and ferrous ions. As shown in Figure 3, the potentiometric titration curves of the CAT and AA complexes with Fe(II) ions are plotted as pH versus the added volume of alkali. The average number of protons linked with CAT and AA were calculated by the equation. The formation curves of the complex equilibriums were obtained by plotting the degree of the complex formation (an average number of ligand molecules attached per metal ion) against the negative logarithm of the concentration of the non-protonated ligand (Figure 4) and calculated using the Irving and Williams [30] equations.

The value of $\log K^1_H$ is the pH value corresponding to $n_H \approx 0.5$. The obtained result for AA and CAT is presented in Table 1. However, they demonstrated that AA and CAT have two association constant. This is due to the difference in the medium and ionic strength used.

	$\log K^1_H$	$\log K^2_H$
Catechol(CAT)	10.45	2.02
Ascorbic acid(AA)	10.61	2.2

Table 2: The stability constants of the proton-ligand of CAT and AA.

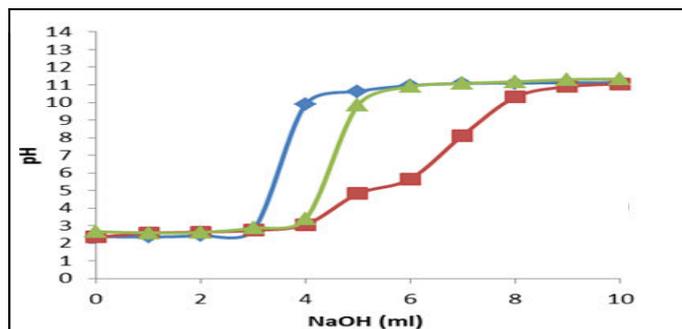


Figure 3: Potentiometric titration curves of binary complexes of AA and CAT at $37.0 \pm 0.1^\circ\text{C}$.

Note: (\blacklozenge) HCl, (\blacksquare) Fe(II)+(CAT), (\blacktriangle) Fe(II)+(AA).

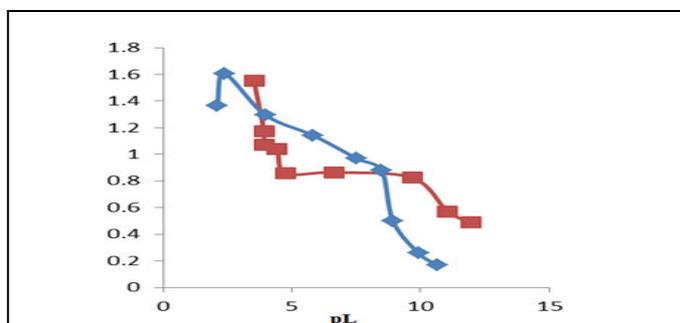


Figure 4: Potentiometric constant curve of binary complexes of AA and CAT at $37.0 \pm 0.1^\circ\text{C}$.

Note: (\blacksquare) Fe (II) + (AA), (\blacklozenge) Fe (II) + (CAT).

	$\log K^1$	$\log K^2$
Catechol	2.81912	8.89901
Ascorbic acid	3.524513	11.58832

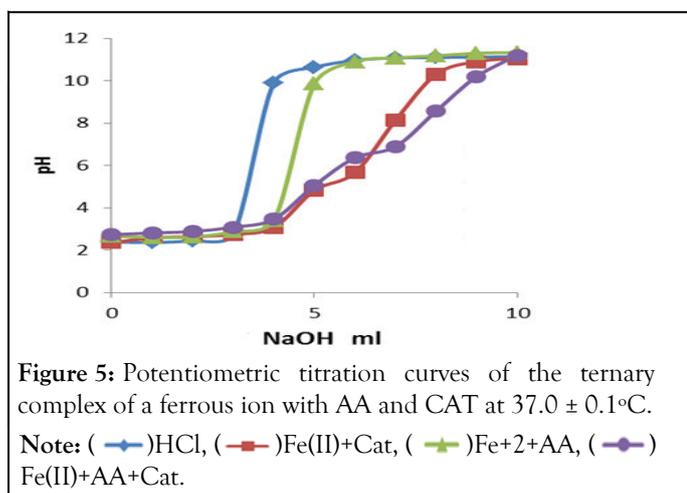
Table 3: Stability constants of Fe(II) with CAT and AA.

Table 3 shows the stability constants of the binary complexes formed between binary complexes of AA and CAT and the ferrous ions at ($37.0 \pm 0.1^\circ\text{C}$). It was found that the stability constant of the ferrous complex of AA is higher than the ferrous

CAT complex. Such behavior of AA may be due to its bidentate structure that coordinates through the oxygen atom of two hydroxyl group, forming a stable five-membered chelate ring as illustrated in Figure 5.

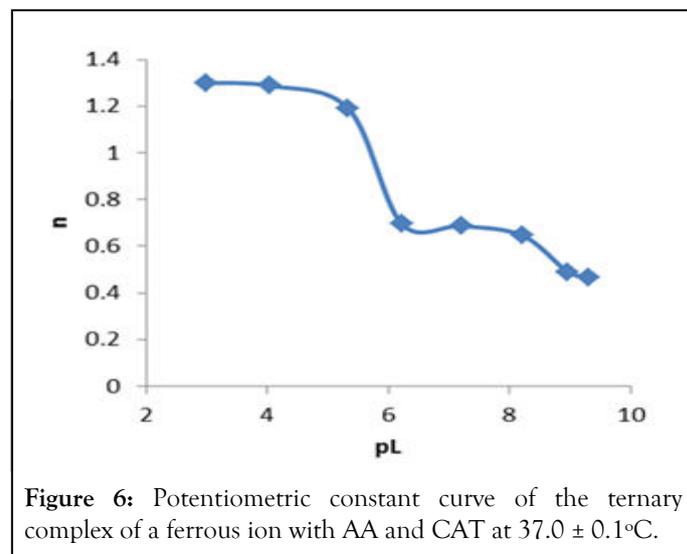
Ternary complex

The mixed ligand (ternary) complexes were determined by the study of potentiometric titration curves. These titration curves strongly overlap with the titration curves of the 1:1 binary Fe(II) (AA) at low pH values due to the high pH value of the ternary titration curve which depends on the nature of both the ferrous ions and the two ligands. In the present study, the addition of the two ligands was stepwise. It was deduced that CAT interacts first with the Fe(II) ion, followed by the interaction with the AA, as the ternary complex formation in stepwise complexation equilibrium.



By putting the value $n=0.5$ in equation; we obtained $\log K_1 = pL$. Similarly by putting the value $n=1.5$ in the equation we obtained $\log K_2 = pL$. It means if we plot a graph between n and pL then the corresponding values of pL at n equal to 0.5 and 1.5 $\log K_{1H}$ and $\log K_{2H}$ gives and respectively. The stability constants of binary metal-ligand were calculated and are presented in Table 3.

The stabilities of ternary complexes can be quantified by the calculation of $\Delta \log K$. The pH titration technique of Irving and Rossotti [16] and its modified form were employed in the present study to determine the stability constants of the ternary complex. The potentiometric titration curves for [Fe(II)-CAT-AA] in a 1:1:1 molar ratio at 310.15K 0.001M are shown in Figure 6. The primary complex curve (free acid+Fe(II)+AA) and mixed ligand curve (free acid+Fe(II)+CAT+AA) overlap each other up to $pH=5$. This indicates that in this pH range when primary ligand combines with metal, a combination of secondary ligand does not take place (Table 4).

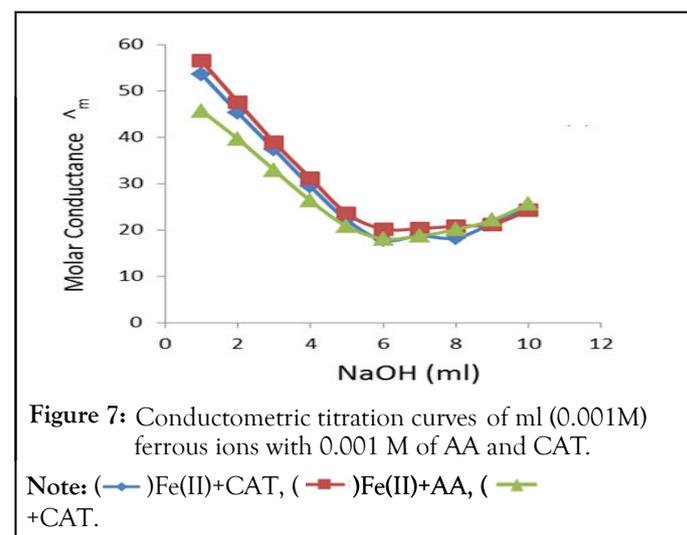


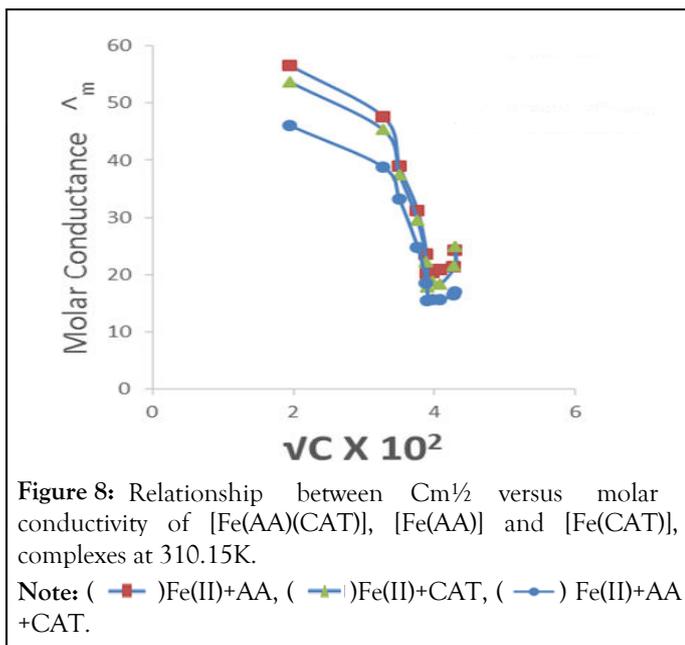
Ternary complex	$\Delta \log K$
[Fe(AA)(CAT)]	2.734

Table 4: The stability constants of [Fe (AA) (CAT)].

Conductivity of binary and ternary complexes

The molar conductance (Λ_m) values were calculated using equation [9]. The limiting molar conductance (Λ_m°) at infinite dilutions were estimated for all metal solution in the presence of the ligand (AA) by extrapolating the relation between Λ_m ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$) and $C_m^{1/2}$ to zero concentration equations [10] (Figure 7 and 8).





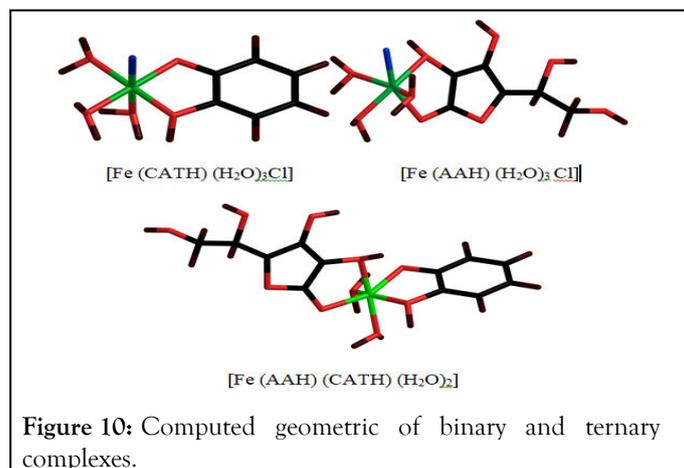
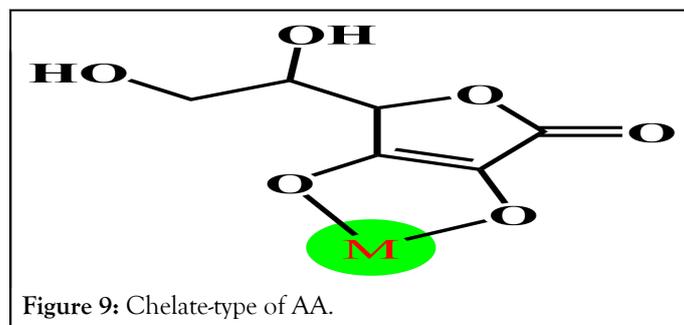
From the Figure 7 and 8, it was noted that the conductivity decreases with increased concentration, which probably corresponds to the neutralization of AA. and CAT ions resulting from the formation of the Fe(II) binary complex. Between 8< ml of added NaOH <11, the conductance increases slightly due to the formation of the ternary complex and is associated with the release of two protons from the secondary ligand. In addition, the molar conductance values indicate that the complexes are neutral.

DFT calculations

DFT calculations were performed using Dmol3 program to determine the binary ferrous ion associated with AA and CAT in which the metal ligand ratio (M:L) is 1:1, or ternary complex of $[\text{Fe}(\text{II})(\text{AA})(\text{CAT})]$ with molar ratio 1:1:1, respectively.

Structurally, AA, H_2A (Figure 9) is a weak dibasic acid, the monoanion (HA) forms at pH 4–5 with deprotonation of $\text{O}(3)\text{-H}$ and the dianion (A) forms at pH 11–12 with deprotonation of the $\text{O}(2)\text{-H}$ [17]. The mono-anionic form is more stable due to the delocalization of the negative charge between the oxygen atoms at the 1- and 3-positions [17,18]. Although AA has several donor atoms capable of metal complex formation, the interaction of HA with metals mainly occurs monodentately through the $\text{O}(3)$ atom [17,19,20] or by chelation via $\text{O}(3)$ and $\text{O}(2)$ [17,21,22], as shown in Figure 9, depending on the nature of the metal cation and the pH of the solution [17]. Thus, the attempt to do the (DFT) calculation on mono-anionic bidentate ferrous complex of AA, $[\text{Fe}(\text{AA})(\text{Cl})]$, which is supported by low conductivity of formed neutral complex in solution. In addition, CAT considered as bidentate mono-anionic ligand as demonstrated in Figure 10.

Frontier molecular orbitals HOMO/LUMO and the energy gap (ΔE) are used to predict the reactivity of molecules [23]. The ΔE (HOMO-LUMO) (equation 11), is essential factor that defines the reactivity of molecules [24]. Generally, large values of the energy gap (ΔE) imply high electronic stability of the molecule [24]. However, the low values imply that it will be easier to remove an electron from the HOMO orbital to LUMO, and then less stable [25].



Spectrophotometry study of lack tea and AAb

UV-Vis spectroscopy is a popular powerful analytical technique used for routine analysis, due to its cost-effectiveness and simplicity. It has been used to study its interaction with ferrous ions in the presence of AA.

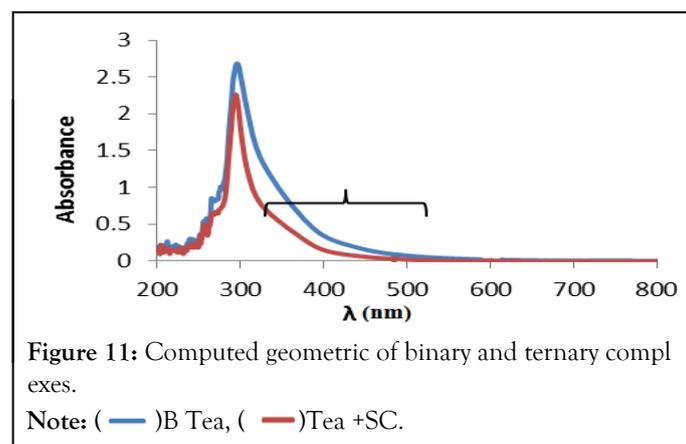


Figure 10 illustrates the absorption spectra of aqueous tea extract in the range of 200-800 nm. However, the spectrum agreed with that spectrum reported previously [26,27], although the separation at the peaks was more pronounced in their spectra due to the methanol solvent which affected the position of the spectral band, the maximum absorption. In Figure 11, the transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ is found within the range of 200-500 nm.

such as Fe (III), it can be reduced to 5-8 [7]. Polyphenols and iron ions can form complexes with iron ions in proportion to iron: polyphenols are 1: 1, 1: 2, 1: 3. The presence of each type of complex in a solution depends on the iron concentration, the binding concentration, the pH of the solution, and the structure of the polyphenols [31].

1:1 M:L	ELUMO- EHOMO	Binding energy (ev)
[Fe(CAT)(H ₂ O) ₃ Cl]	0.084	-104.19
[Fe(AA) (H ₂ O) ₃ Cl]	0.069	-127.49
[Fe(AA) (H ₂ O) ₂] (CAT)	0.3956	-180.2

Table 5: Energy gap and binding energy of computed complexes.

It turns out that the area above 500 nm does not contain any $d \rightarrow d$ transitions, after adding AA to the black tea. The disappearance of the $d \rightarrow d$ transitions after adding AA is strong evidence that the iron-polyphenols complexes do not take place in the presence of AA [29]. This behavior is attributed to the low pH value in the

However, the $\pi \rightarrow \pi^*$ transitions resulting from the successive double bonds such as the one in the vinyl ring. In addition, the $n \rightarrow \pi^*$ transitions correspond to the absorption of the C=O chromophore in catechins and methylxanthines containing caffeine, theobromine, theophylline and flavins in black tea as a result of a fermentation process of green tea. Their electron absorption can be evaluated in the range of 380-460 nm [26,28] can be seen as overlapping peaks in the ranges of 400-300 nm, and another band appears around 500-400 nm has a poor absorbance associated with the presence of the phenolic compounds present in the tea extract [27].

$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$

The energy gap (ΔE) and the binding energy presented in Table 5. The energy gap indicates that the ferrous-AA complex is more stable than the ferrous-CAT complex. Moreover, the ternary complex is more stable than the binary complexes, which is in good agreement with the potentiometric measurements.

presence of AA, as well as the role of AA as a reducing agent that prevents the transformation of ferrous ions into ferric ions [9]. The flavan ring system consisting of three benzene rings is typically the most abundant presence of the bulk of polyphenols in food [7,30]. Protonated polyphenols form high charge density oxygen centers that have the high potential to form bonds with metal ions [7]. Typically, polyphenols are deprotonated at the pH range 9-10 but in the presence of some metal cations,

Figures 12 and 13 show the spectra of black tea in the presence of AA in the range of 200-900 nm.

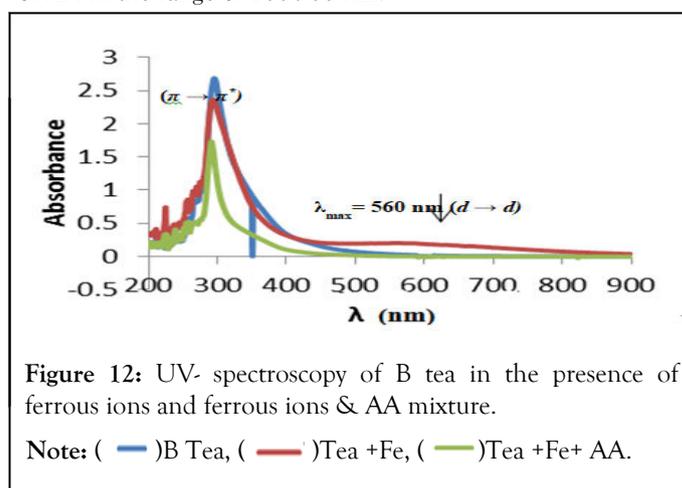


Figure 12: UV- spectroscopy of B tea in the presence of ferrous ions and ferrous ions & AA mixture.

Note: (—)B Tea, (—)Tea +Fe, (—)Tea +Fe+ AA.

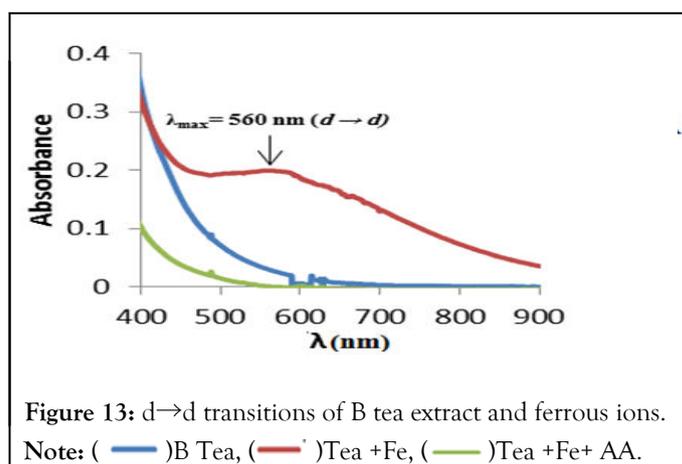


Figure 13: $d \rightarrow d$ transitions of B tea extract and ferrous ions.

Note: (—)B Tea, (—)Tea +Fe, (—)Tea +Fe+ AA.

At a slightly acidic pH (pH=5-6.5), each iron atom is usually bound to two or three CAT molecules, forming complexes of blue-purple color [23]. At a more acidic pH (<4 pH), polyphenols bind with iron in a 1: 1 ratio, forming bluish green complexes [30]. At a pH of 8 and above, iron polyphenols 1: 3 are predominant and are red in color [30,31]. The spontaneous oxidation that occurs at neutral pH is characterized by the rapid oxidation of Fe (II)-polyphenols to Fe(III)-polyphenols [32].

CONCLUSION

The stability constants of the binary and the ternary complexes formed from ferrous ion with catechol and ascorbic acid at equilibrium were studied by potentiometry and conductivity measurements. The stability constants (log K) were calculated for the prepared complexes to be on the order: [(Fe (AA))>[(Fe (CAT)], thus, iron binary complexes with ascorbic acid were considered to be more stable than the iron complexes with catechol according to their stability constants. The ternary complex was prepared and its stability constants and experimental $\Delta\log K$ coefficients were calculated. The positive value of $\Delta\log K$ indicates that the ternary complex is more stable than both of the binary complexes. When the Black tea was reacted with ascorbic acid, the absence of d→d transmission was observed in the electronic Uv-Vis spectrum. Theoretically, stability of complexes were calculated based on the energy gap values which indicated that the ferrous-AA complex is more stable than the ferrous-CAT complex. Moreover, the ternary complex is more stable than the binary complexes, which is in good agreement with the potentiometric measurements.

ACKNOWLEDGMENT

The authors wish to acknowledge the chemistry department-Sebha University for providing the necessary facilities to carry out the studies.

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