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Evaluation of Stability constant of Binary complex of Tannic Acid with Fe(II) in Aqueous Solution: Potentiometric Study

Nouria A. Shnin[1], Aziza K. Haiwdi[2], Mohamed Zidan[3] and Aisha A. AL-Abbasi [*]

***Corresponding author:** ais.alabbasi@sebhau.edu.ly, Department of Chemistry, Faculty of Science, University of Sebha, Libya.

[1, 2, 3] Department of Chemistry, Faculty of Science, University of Sebha, Libya.

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Abstract
Tannic acid as a polyphenol has biological and pharmacological activities, as well as its ability to bond to a wave of transition metals. In this study, the protonation equilibria of the tannic acid were determined and used for determining the stability constants of the binary complexes formed with iron (II) ions in the aqueous medium under the experimental conditions by the potentiometric method using Irving and Rossotti equation, where Stability constant was 3.205 for Fe(II)–tannic acid complex. In contrast, Fe(II) formed complexes with tannic acid of various stoichiometries, which in the 1:1 molar ratio at pH = 11.24. Furthermore, the ionic strength and the influence of temperature on the stability of the complexes are investigated, where stability constant in the presence of 0.1 M NaCl (ionic strength) of binary iron-Tan complex equal 3.254, and at different temperatures were log K1= 3.156 at 298.15 K, log K1 = 3.205 at 310.15 K, and log K1= 3.256 at 313.15 K.

Keywords: Ferrous ions; Formation constant; Binary complexes; potentiometry; tannic acid

INTRODUCTION

The majority of most living organisms depend on iron as a necessary mineral element since it is considered essential to all life and existence. It can be found in most nutrition bases (Abbaspour et al., 2014). The right amount of gin is produced by the body to minimize iron production; too much or too little causes an imbalance in the body. As the protein that carries oxygen to all of the body's cells and organs, hemoglobin needs iron to function (McGee, 2017). It also functions as a catalyst for many other enzymes, including catalase (Kadiiska et al., 1995). A newborn child's body has 0.5 grams of iron, compared to 4-5 grams for an adult male and roughly 3 grams for a female's body (Moustarah & Daley, 2024). The majority of this amount 65% is found in red blood cells, specifically in hemoglobin. The remaining 25% is found in iron reserves, such as ferritin or hemosiderin, and the other 10% is found in muscles, specifically in myoglobin (McDermid & Lönnerdal, 2012, Kaufman et al., 2024).

Many foods include two different forms of iron: non-heme iron, which is found in grains, vegetables, fortified foods, nutritional supplements, eggs, almonds, and green vegetables, particularly spinach; and heme iron, which is associated with hemoglobin and myoglobin (Hurrell & Egli, 2010). Heme iron is bioavailable (15–35%) and is not significantly affected by dietary variables, but non-heme iron absorption is significantly lower (2–20%) and extensively influenced by other food components (Piskin et al., 2022). However, in most meals, non-heme iron is far more plentiful in the diet than heme iron. Despite its lower bioavailability, non-heme iron makes a greater contribution to iron nutrition than heme iron. The substances that inhibit iron absorption comprise polyphenols, calcium, and photic acid (Ems & Huecker, 2019).

Many types of plant material include tannin. Galatannin is the chemical component that makes up most natural tannin (Cotoraci et al., 2021). It contains a complicated compound that is fundamentally made up of one glucose molecule bound to up to five digallic acid molecules, as seen in Figure 1 (Fu & Chen, 2019). The tannin molecule hydrolyzes in a water solution to produce glucose and digallic acid. Tannic acid's acidic qualities are derived from the carboxyl hydrogen found inside the digallic acid molecule. One particular kind of tannin, a kind of polyphenol, is tannic acid. The various phenol sets in the molecule are the source of its low acidity (pK_a of about 6). This formula is equivalent to decagalloyl glucose. The above system represents the tannic acid utilized in those tests, which has a molecular weight of 322 (Fu & Chen, 2019). To reduce bleeding, people apply tannic acid to the area where they have been exposed, especially to cold sores and fever blisters, diaper rash and prickly heat, poison ivy, ingrown toenails, sore throat, sore tonsils, spongy or receding gums, and skin rashes.

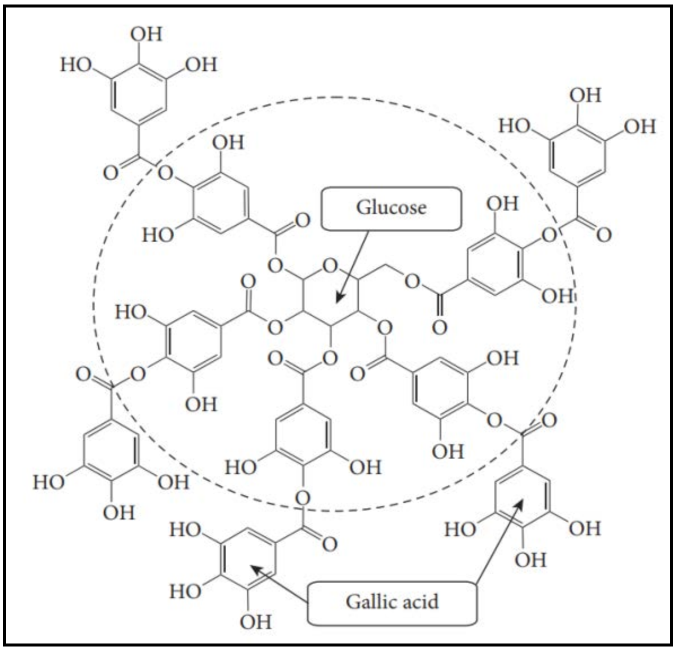


Figure (1). Configuration of tannic acid (Fu & Chen, 2019)

Oral tannic acid treatment is available for bleeding, dysentery, prolonged diarrhea, bloody urine, aching joints, persistent coughing fits, and cancer (Chen et al., 2022). Over the past ten years, there has been a growing usage of tannic acid (Tan), an antioxidant present in plants, in biomedical research.(Maharani et al., 2022). Tannic acid extracted from the galls of oak trees has been used for ages in various important applications (Maharani et al., 2022). Tan's application in Tan is based on its hydrogen bonding properties with proteins and other biomolecules, as well as its abundance of hydroxyl groups, which provide it versatility (Baldwin & Booth, 2022). Huge, subdued-colored molecules that exhibit colloidal behavior can be found in combinations of tannic acid and iron (Ahmad, 2014).

There are some Factors affecting the stability of metal compensation such as solvent, temperature (which has an impact on the values of stability constant) and the nature of ligands. In a prior study, the potentiometric approach was to estimate the stability constants of binary complexes generated from iron (II) ions with tannic acid as our controversial motive for exploring the behavior of metal ions in aqueous solution (Al-abbasi A., 2023, Al-abbası A., 2023, Belkher, 2019 , Al-abbasi et al., 2022, Suhud et al., 2015, Khalifa, 2018, Dnkm et al., 2024). Additionally, the exploring the effect of temp. and ionic strength of NaCl on the formed complex and calculating thermodynamic parameters.

MATERIALS AND METHODS

Chemicals and Instrumentations

All chemicals and materials were of reagent grade or the highest quality commercially available and were used without further purification: Tannic acid (BDH Chemicals, 99%), ferrous Chloride (Carlo Erba, 99.8 %), Sodium Hydroxide (Shandong China), 98.8%), Sodium Chloride (BDH Chemicals, 99.7%), Hydrochloride (Scharlau chemise, 36%). The devices used are all from well-known companies: Balance (Mettlertoledo/Al204), Thermostat Water Bath (Grant Instrument, England), Conductivity/ pH-meter (Thermo Electron/Orion3 Star (PH Benchtop)/USA).

Preparation of Standard Solutions

Ferrous chloride (0.176 g) was dissolved in a standard beaker (100 mL), and the volume was filled with distilled water (deionized) up to the mark to obtain a concentration of 0.01M. Other concentrations of 0.001 M and 0.005 M were obtained. Tannic acid (0.176 g) was dissolved in a standard flask with a capacity of 100 mL, and the volume was filled with distilled water up to the mark to obtain a concentration of 0.01 M, from which other concentrations (0.005 M) were obtained. 0.001 M. A solution of (0.1 M) sodium hydroxide was prepared by dissolving the requisite quantities (2 g) with distilled deionized water. The solution of sodium hydroxide was standardized by titrating against the standard oxalic acid solution. The solution was used as the titrant for the pH-metric titrations. Sodium chloride solution (0.1 M) was prepared by dissolving 1.461 g of NaCl in a standard 250 mL beaker and filling the volume up to the mark with distilled (deionized) water.

Effect of temperature and ionic strength on the formation of binary complex

The temperature effect on the binary and ternary complexes was studied pH-metrically at temperatures of 293.15 K, 298.15 K, 303.15 K, 310.15 K and 313.15 K and 0.004 M metal ion concentration. The stability constant was determined at each temperature, and its values can be correlated with ΔG (free energy), ΔH (enthalpy), and ΔS (entropy). The potential and conductivity measurements were performed in the presence of a strong electrolyte of NaCl. This study was conducted to determine the effect of adding 0.1 M sodium chloride (NaCl) on the formation of the complexes at a temperature of 313.15 K.

RESULTS

Formation constants of the ligands

Dissociation constants of Ascorbic acid, Glutamine, and Tannic acid were investigated by titration titrations using sodium hydroxide. The following curves were constructed using the titration data:

i. Free Acid (HCl) Curve
ii. the free acid+ Tannic acid (HCl+ Tan) Curve.

$$HL \overset{K_1^H}{\rightleftarrows} H^+ + L^- \quad (1)$$

$$K_1^H = \frac{[H^+][L^-]}{[HL]} \quad (2)$$

Values of n_A (average number of protons attached to each ligand) were determined according to Irving and Rossotti as shown in Eq. 3:

$$\bar{n}_A = Y + \frac{(V' - V'') \times (N - E^\circ)}{(V^\circ - V') \times T_L^\circ} \qquad 3$$

Where: $\bar{n}_A$ is the average number of protons bound per not complex bound ligand molecule, y is the number of the replaceable hydrogen atoms from the ligand, V^O is the initial total volume of solution, V' and V'' are the volume of alkali required to attain the same pH in the acid curve and same pH in the (acid + ligand) curve, respectively, N is the concentration of alkali, E^o and T_L^O are the initial concentration of HCl acid and the total ligand concentration, respectively. The pH value corresponding to n_A= 0.5, 1.5, 2.5, 3.5, and 4.5 is represented by the values of $\log K_1^H$, $\log K_2^H$, $\log K_3^H$, and $\log K_4^H$ (the ligands' proton dissociation constants) as shown in (Table 1).

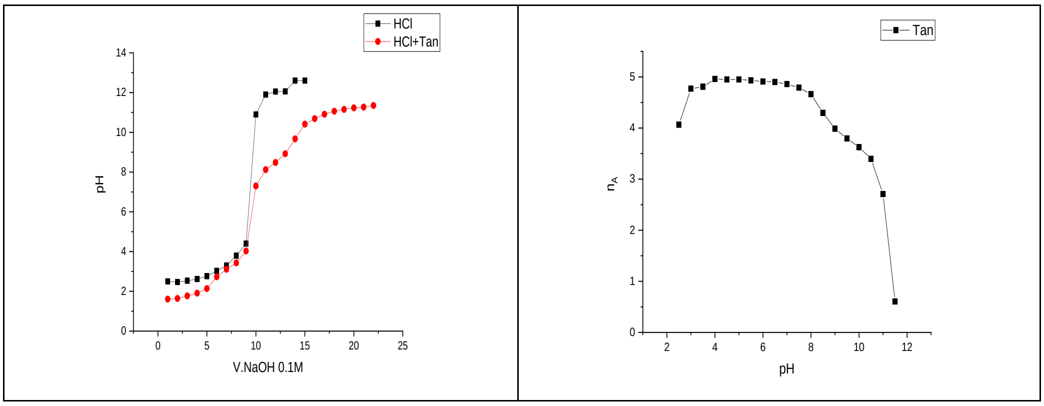


Figure (2). Potentiometric titration curves and Protonation constant curves of 0.01M Tannic Acid at 310.15 K

According to the Irving Rossetti equation, Figure 2 shows how the correlates' dissociation constants can be calculated from the pH value corresponding to their n_A values at (0.5, 1.5, 2.5 values). For Tannic acid, the $\log K_1^H$, $\log K_2^H$, $\log K_3^H$, and $\log K_4^H$ values are given by the pH values corresponding to 1.5, 2.5, 3.5 and 4.5 values. As for Tannic acid, it shows similarity in the recorded values, but a difference appears in the number of protons given, in which the results recorded in this study showed that the Tannic acid gives four protons, while the previous study showed that it gives only two protons (Zheng et al., 2016).

Table (1). Values of dissociation constants of Tan at 310.15K

298.15 K	310.15 K	313.15K
K_{a1}=11.65	K_{a1} =11.51	$K_{a1=}$ 12.5
K_{a2} =11.08	K_{a2} =11.3	K_{a2} = 12. 0
K_{a3} = 10.15	K_{a3} = 11.08	K_{a3}= 11.15
K_{a4} = 8.05	K_{a4} = 10.35	K_{a4} = 9.1
K_{a5} = 6	K_{a5} = 8.2	K_5= 7.0
K_{a6}=/	K_{a6} = 2.4	K_6= 2.3

Binary complex of ferrous Tennate

The stability of complexes of iron (Fe^{+2}) with different bioactive Tannic acids was studied by the potentiometric method. This study was done by forming this complex in an aqueous solution in the presence and absence of ionic strength of sodium chloride at a body temperature of 37 °C under certain conditions of concentration. Formation constants of Iron (Fe^{+2}) binary complex Tannic acid were studied by potentiometric titrations using sodium hydroxide. The following curves were constructed using the titration data:

1) Free acid curve

2) free acid + Tan
3) free acid+ Tan + Fe^{+2}

Following equations were used to compute $\bar{n}$ (average number of ligand molecules attached) and p_L (free ligand exponent) as revealed by Irving and Rossotti (Almbrok, 2023; Irving & Rossotti, 1954; Irving, 1953):

$$n_L = \frac{(V'' - V''') \times (N - E^{\circ})}{(V^{\circ} - V'') \times T_M^{o} \times \bar{n}_A} \qquad 4$$

$$pL = \log\left[\frac{1 + pK_1^H[H^+] + pK_1^H \cdot pK_2^H([H^+])^2}{T_L^{\circ} - \bar{n}T_M^{\circ}} \times \frac{V^{\circ} + V'''}{V^{\circ}}\right] \qquad 5$$

Where $\bar{n}_A$ is the average number of protons bound per not complex bound ligand molecule, V^o is the initial total volume of solution, V', V'' and V''' are the volume of alkali required to attain the same pH in the acid curve, same pH in the (acid + Tan) curve and volume of alkali required to attain the same pH in the (acid+ Fe^{+2} + Tan) curve respectively, N is the concentration of alkali, E^o and T_L^o are the initial concentration of HCl acid and the total ligand concentration, respectively, T_M° is total metal ion concentration.

The stability constant of ferrous binary complexes with Tan ligands were investigated potentiometrically. The effect of changing the concentration of ferrous ion on stability constants of binary complexes were investigated by using different concentrations of 0.001 M, 0.005 M and 0.01 M of ferrous ion at 310.15 K. According to Irving and Rossotti calculations; the $\bar{n}$ and p_L values at the ferrous ions concentration of 0.005 M and 0.001 M were all negative. As a result, the formation constants at that concentration could not obtained and the 0.01M was chosen for studying the formation constant of ferrous binary complexes of Asc, Glut and Tan ligands. The stability constants of the ferrous tannate complex at 310.15K were found to be 3.205 at pH 11.14

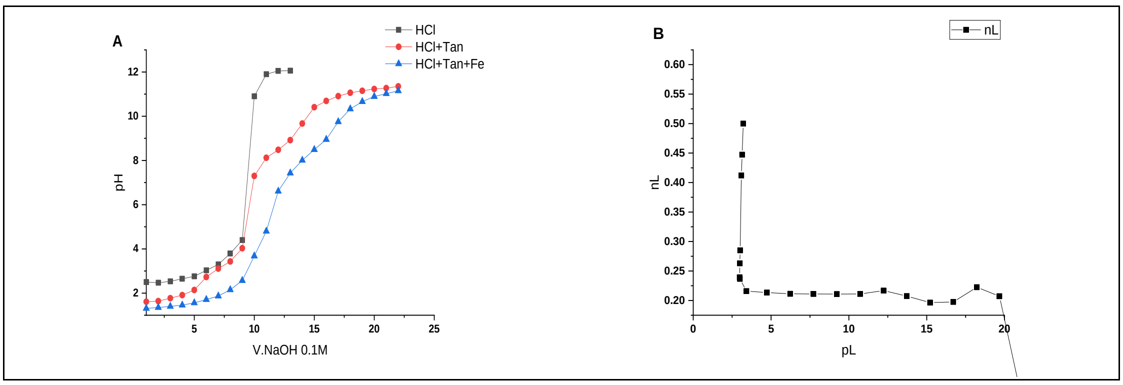


Figure (3). Potentiometric titration (A), and Protonation constant Curves (B) of ferrous- Tan complex at 0.01M

The following general observations can be made: (i) The metal solutions employed in the present investigation are dilute (1×10^{-2} M); (ii) Proton release upon the formation of the metal ion complexes with the ligand was indicated by shifting the metal ion titration curves to the right-hand side of the ligand titration curve along the alkali volume axis (Al-Saidi et al., 2020). The Tannic acid binary complex, only shows one formation constant at pH = 11.24. the other formation constant might be found at pH higher than 13, which is cannot detected in our experiments pH.

Curves (Figure 3) and equations (4 & 5) were utilised to determine the values of nL, pL. The metal ion titration curves were moved to the right-hand side of the ligand titration curve along the alkali volume axis, referring to proton release upon formation of the metal ions complexes with the ligand [15]. The tannic acid binary complex only displays one formation constant at pH = 11.24 and log K = 3.205; the other formation constant may be found at pH higher than 13, which is not detected in our experiment's. The values of nL, pL obtained for the iron-Tan stoichiometric system indicate the formation of 1:1 complexes, and they were related to the following equilibrium equations 6 & 7:

$$M^{+} + L^{-} \xrightleftharpoons{K_1} ML \qquad 6$$

$$K_1 = \frac{[ML]}{[M^{+}][L^{-}]} \qquad 7$$

Protons attaching to Tan's hydroxide group with metal ions to create complexes is related to the log K_1 value.

Ionic strength

To study the effect of ionic strength on the dissociation constant of Tan and the stability constant of its corresponding complex; a fixed concentration of each ligand (0.01 M) was chosen, and the dissociation constants were studied in the presence of a fixed concentration of sodium chloride (0.1 M) by titrations with sodium hydroxide, where the titrations data were used to build the following curves: Free Acid + NaCl, free acid + Tan acid + NaCl, The free acid + Tannic acid + Fe^{+2} + NaCl as shown in Figure 4.

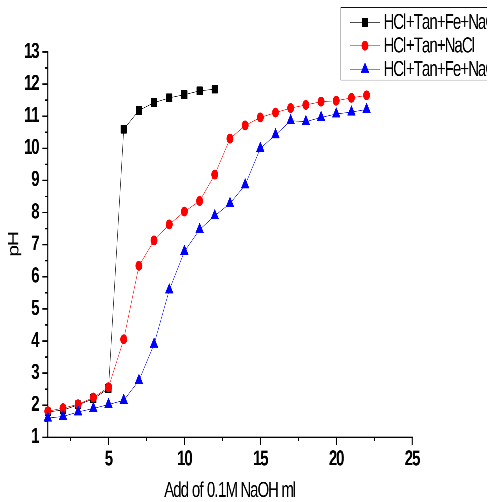


Figure (4). Potentiometric of Tan and its complex in the presence of 0.1M NaCl at 310.15K

Figure 4 shows the potentiometric titration curves in the presence and absence of NaCl by using Irving Rosseti's method. The obtained values of the dissociation constants are presented in Table 2.

Table (2). Dissociation constant and stability constant of Tan and ferrous tannat at 310.15K in the presence and the absence of NaCl

Comp.	Log K_a	Log K_a in 0.1M NaCl
Tan	K_{a1} =11.51 K_{a2} =11.3 K_{a3} = 11.08 K_{a4} = 10.35 K_{a5} = 8.2 K_{a6} = 2.4	K_{a1} =11.45 K_{a1} = 11.08 K_{a2} = 10.15 K_{a3} = 8.1 K_{a4} = 6.41
Ferrous-Tan	$\log k_1$ =3.205	$\log k_1$=3.254

The Table shows the values of dissociation constant and stability constant for ligand and binary complexes and the effect of ionic strength, which were determined according to Irving Rossotti's method. Figure 5 and Table 2 demonstrate how the protonation constants of Tan decrease in the presence of ionic strength, hence decreasing the degree of ligand dissociation, by looking at the dissociation and stability constants for ligand and binary complexes. Additionally, the stability constants of the metal ion in complexes with ligand are larger than those of the complexes without ionic strength, indicating a stronger ligands between the metal and Tan.

Effect of temperature

The effect of temperature on the binary complexes of Tan with iron ions was investigated with a constant concentration of 0.01 M and at different temperatures, where three temperatures were chosen (298.15K, 310.15K, and 313.15K) as shown in Figure 6, where iron-Tan complexes were formed at all temperatures due to convergence and spacing of the Tan curve and iron with Tan curve then convergence there again.

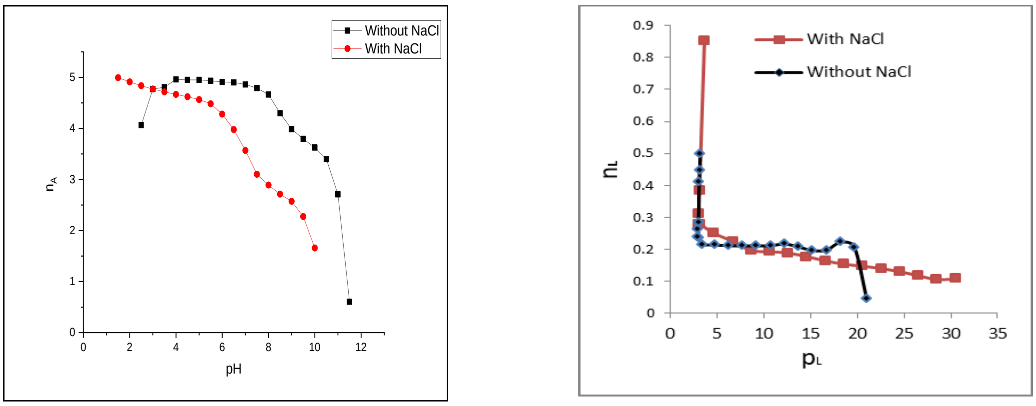


Figure 5: Potentiometric titration (A), and Protonation constant Curves (B) of ferrous-ASC, Glut, TA complexes at presence 0.1M NaCl, 310.15 K and 0.01M

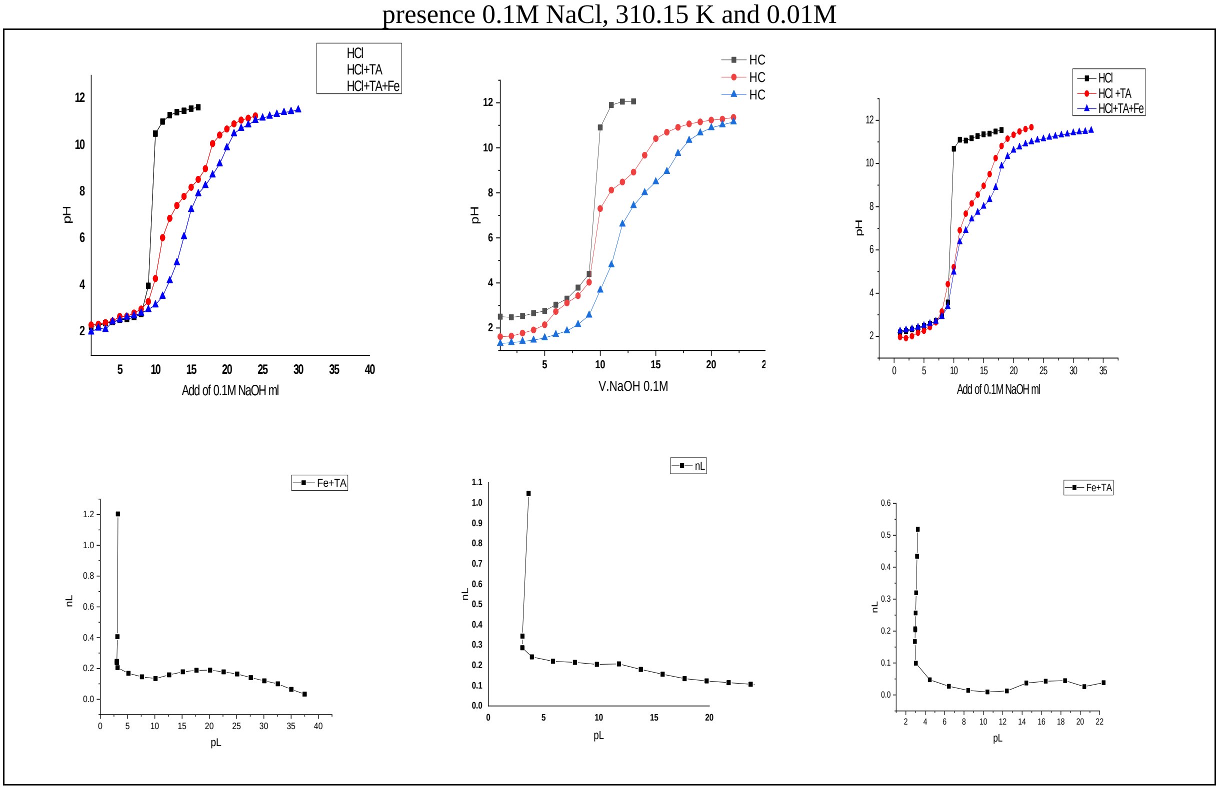


Figure (6). potentiometric titration and Formation constant curves of binary ferrous complexes at 298.15K,313.10K

Effect of temperature

The effect of temperature on the binary complexes of Tan with iron ions was investigated with a constant concentration of 0.01 M and at different temperatures, where three temperatures were chosen (298.15K, 310.15K, and 313.15K) as shown in Figure 6, where iron-Tan complexes were formed at all temperatures due to convergence and spacing of the Tan curve and iron with Tan curve then convergence there again.

Analyzing Figure 6 and Table 3, it can be observed that metal ions with Tan produce a particular type of metal–ligand complexes: 1:1, with the absence of complexity being 1: 2 and the pH being independent at varying temperatures, The formation constant values iron-Tan complexes tend to increase with temperature as a result of increased interference between the iron and Tan ions, leading to higher nL values.

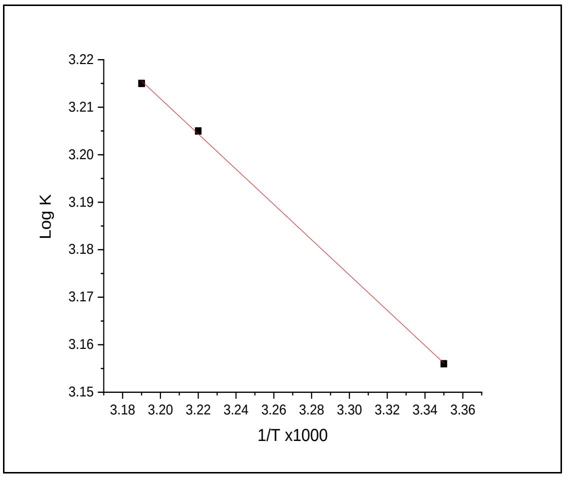
Table (3). Formation constants of binary iron complexes at different temperature

Comp.	298.15 K	310.15 K	313.15 K
Tan	K_{a1}=11.65	K_{a1} =11.51	K_{a1}= 12.5
	K_{a2} =11.08	K_{a2} =11.3	K_{a2} = 12. 0
	K_{a3} = 10.15	K_{a3} = 11.08	K_{a3}= 11.15
	K_{a4} = 8.05	K_{a4} = 10.35	K_{a4} = 9.1
	K_{a5} = 6	K_{a5} = 8.2	K_5= 7.0
	K_{a6}=/	K_{a6} = 2.4	K_6= 2.3
Iron-Tan	log K_1=3.156	log K_1=3.205	log K_1=3.215

Thermodynamic functions are the true measure of the interference strength between reactants and the nature of the studied system. This study was based on the results obtained from log K calculations at different temperatures, enthalpy values were calculated using the van't-Hoff relationship (Almutaleb & Alabbasi, 2023; Kemp, 1987).

$$logK = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{R} \qquad 8$$

By drawing the relation between log K and 1/T, a straight line with slope (-ΔH/2.303R) was given Figure 7, the interception was used to calculate the entropy (ΔS). Where R is the gas constant and T is the temperature.



Figure(7). Application of Van't-Hoff relationship to iron - Tan complexes

Additionally the value of the change in free Gibbs energy (ΔG) was calculated through the relationship 9.

$$\Delta G = -2.303\ RT \log K] \qquad 9$$

The values of thermodynamic functions ΔS, ΔH, and ΔG for Tan with the metal ion complexes that were calculated are listed in Table 4.

Table (4). Values of thermodynamic functions of iron ion complexes at different temperatures and 0.01M

Thermodynamic functions	Values	
R^2	0.9998	
ΔH (KJ/mol)	+7.10741±0.0	
ΔS (J/mol . k)	+36.57852±0.0	
ΔG (KJ/mol)	298.15K	-18.01672
	310.15K	-19.03284
	313.15K	-19.27690

Table 4 shows the values of the thermodynamic functions of the binary iron complexes with the correlates under study. From this table, the following can be noted: I) The application of the Van't-Hoff equation gave a good linear relationship indicating that the value of the correlation coefficient is (0.999) for ferrous Tannic acid. II) A negative value of ΔG indicates that the reaction occurs spontaneously and its value decreases with the increase in temperature. III) ΔH values indicate that the reaction is endothermic. IV) positive ΔS values indicate that the interaction between ferrous and ligands is a random process

CONCLUSION

In this research, the stability constant (log K) and stoichiometric of these complexes were also investigated by the Potentiometric method, where the tannic acid binary complex only shows one formation constant at pH = 11.24 and log K = 3.205. The iron-Tan stoichiometric system indicates the formation of complexes was kept in the ratio 1:1. The Stability constants for all binary complexes increase with the increase of temperature; while they decrease in the presence of ionic strength the experimental data for thermodynamics indicates that the value of free energies (ΔG) of formation of the binary complexes becomes more negative with an increase in temperature. This shows that the complex formation is a spontaneous process and spontaneity increases with temperature, the enthalpy (ΔH) values indicate the endothermic nature of the complication reaction and explain the effect of temperature on the values of formation constants, and the entropy (ΔS) values indicate that the complex formation is (random process and randomized increases with temperature.

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