International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2016): 79.57 | Impact Factor (2015): 6.391

Thermodynamic and Kinetic Study for the Interaction of Ascorbic Acid with Nickel (II) Ion by Spectrophotometric Methods

Alaa Abd AL-Zahra

Department of Chemistry, College of Science, University of Baghdad, Jadiria, Baghdad, Iraq

Abstract: ***The aim of this paper was study the interaction between ascorbic acid with Nickel (II) by the application of UV-Visible spectroscopic method at four different temperatures (293, 298, 303, 308) K. The change in absorbency improves the complexion between acid and metal ion. The stoichiometry of the interaction was determining by continuous variations methods. The thermodynamic parameters (ΔG°, ΔH° and ΔS°) and equilibrium constant were calculated at four different temperatures refer to the hydrophobic interaction between metal and acid. The kinetic study for this interaction follows second order equation with rate constant value of*** 2×10^{-3} ***M*** $^{-1}$***min*** $^{-1}$

Keywords: Nickel, kinetics, thermodynamic, ascorbic acid.

1. Introduction

Ascorbic acid (C6H8O6) is a water- soluble compound. Itis important for biological function, used for synthesis of collagen in tissues, teeth and skin [1-4]. (C6H8O6) molecule has two asymmetric carbon atoms C-4and c-5. In addition to L-ascorbic acid it has D- iso ascorbic acid, D-ascorbic acid, and L-iso ascorbic acid but they are not activity [5-8]. L - ascorbic acid is hetro cyclic lactone ring [9]. Vitamin c is reducing agent and oxidizes reversibly to dehydro ascorbic acid. It is metabolized in liver involved many amino acid, leading to formation of hydroxyl proline, serotonin, hydroxyl lysine [10]. This vitamin is distributed in nature, special in fresh fruits and vegetables such as spinach. This vitamin increases the absorption of folic acid, calcium and iron [11]. Figure (1) shows the structure of ascorbic acid.

Figure 1: Structural formula of ascorbic acid

Nickel is metallic compound which is known as transitional metallic in periodic table. nickel (II) is important oxidation state in biochemistry, it is form many complexes. It is considering as essentials elements in the body because it is helping the body to absorb iron, and prevent anemia through building strong skeletal by strengthening bones, it is found in DNA, RNA means found in every cell in human body. Nickel is found in plants (peas, beans), fish and chocolate, it is help in breaking down glucose which help improvised energy for daily requirement's [12,13].

Huned.Y.J. **2004**. Study of the interaction between mono ammonium glycyrrhizin ate and bovine serum albumin [14]. HunedY.J. **2005**. Stud the interaction between 1-hexylcarbamoyl-5-flurouracil and bovine serum albumin [15]. FahadD.F. (2012) study the interaction of an antioxidant with toxic arsenic, and the thermodynamic and kineticparameter were calculated at different temperatures [16]. Al- Khafaji N. R. study the (2014): study effectiveness of poly phenol of Nutritional origin to protection from metal ion [17]. Al-Rufaie E. M. and Hussain. A.K. (2014): Studies the interaction of Vitamin C and Nickel (II) using polar graphic methods [18].

Al-jubouri M.A. (2015): calculate thermodynamic and kinetic parameter for the binding of heavy metal with drugs [19].

Aim of the project is study the interaction of (vitamin c) and (nickel) by the application of UV-Visible spectroscopic method, the following calculation were done:

a) The stoichiometric ratio of the complexes.
b) The rate constant and the order of interaction.
c) Equilibrium constant and thermodynamic parameters (ΔH°, ΔS°, ΔG°) for the interaction.

Experimental

2.1 Materials

Pure deionized water was supplied from LV- 08 ultrapure water device. All absorption spectra were taken with the UV-Vis spectrophotometer (Cary Varian) EL04103410, using a quartz cell of 1 cm path length. The absorbance of acid and metals were calculated in a wavelength (200-600nm). Nickel nitrate Ni(NO3)2.6H2O was purchased from Analar/ England. L- ascorbic acid C6H8O6 was purchased from HIMEDIA/India.

Nickel stock solution of (10^{-4}M) concentration were prepared by dissolve 0.029gm of Nickel in 100ml water. Ascorbic acid stock solution of (10^{-4}M) concentration were prepared by dissolve 0.0176gm of acid in 100ml water as solvent.

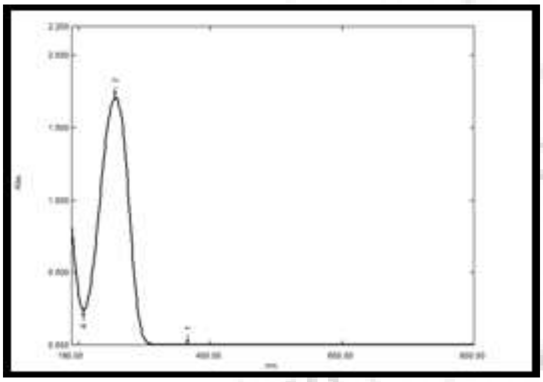
Stoichiometric analysis: The stoichiometry of acid metals complexation was determined by (Jobs method), by a series of ten solutions have a mole fraction in between (0.1 to 0.9) by mixing different volumes of vitamin and metals stock solutions of a concentration (10^{-4}M) for each [20].

2. Results and Discussion

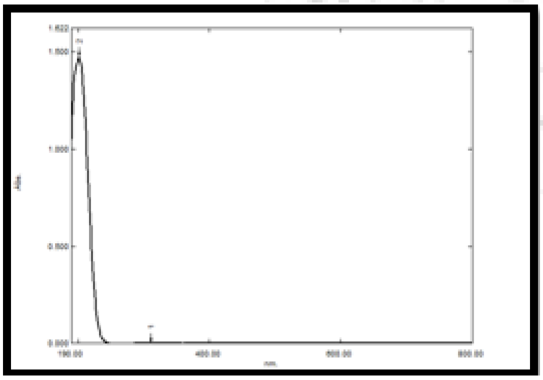
Absorption spectroscopy:

The UV –VIS absorption studies were taken to each ascorbic acid and Nickel and ascorbic acid -Nickel complex. The UV-VIS absorbance showed a shift inλmax (λ max for Ni=202nm, λ max for acid=256nm and λ max for complex=261nm) and aching in the absorbance due to complex formation between metal and vitamin, Figure2(a, b,c)show the absorption spectra of acid and metal.

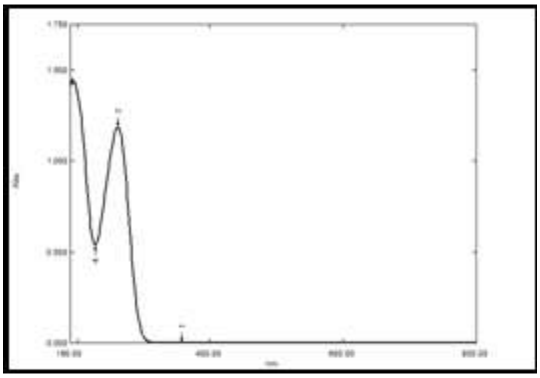
$$\text{acid} + \text{metal} \rightleftharpoons \text{acid metal complex} \quad .... (1)$$



(a)



(b)



(c)

Figure 2 (a): Absorption spectrum of ascorbic acid in pure deionized water
(b): Absorption spectrum of Nickel in pure deionized water.
(c): Absorption spectrum of Ascorbic acid -Nickel complex in pure deionized water.

Stoichiometric analysis

The continuous variation methods used to determine stoichiometry of the complex of ascorbic acid and Nickel (II) [21]. The coordination number n could be calculated from the plot of absorbance ofascorbic acid -Nickel complexat λ max (261nm) against the mole fraction of Nickel. As it evident from the Figure (3) the Job's plot, indicates that the stoichiometric ratio n of ascorbic acid -nickel at (293)K is (1:1).

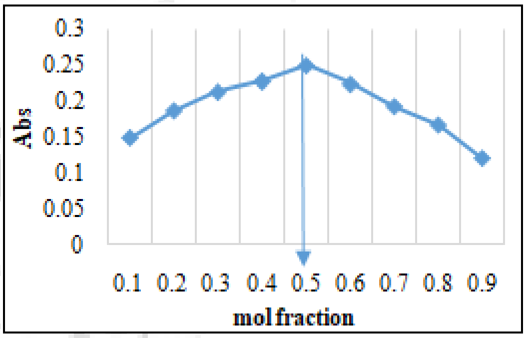


Figure 3: Job's plot for Nickel-ascorbic acid complex

Stability constant (Keq): by continuous variation method, the equilibrium constant can be calculated as show in equation (2) [22, 23]:

$$K_{eq} = \frac{[AMn complex]_{eq}}{[M]_{eq}\ [A]_{eq}} \quad ... (2)$$

$[AM_n\,complex]_{eq}$: concentration of the complex formed between the Nickel and ascorbic acid at equilibrium.
$[M]_{eq}$: concentration of the metal at equilibrium.
$[A]_{eq}$: concentration of the acid at equilibrium.

$$[AM_n\ complex]_{eq} = Absorbance_{(max)} / \varepsilon l .... (3)$$

ε : molar absorptivity of the complex ($cm^{-1}.mol^{-1}$. L).
l: path length (cm).
Absorbance (max) =the maximum absorbance of the complex

The molar absorptivity of the complex was calculated by recording the absorbance of a various concentration of 1:1complex with their stoichiometric ratio, at different temperatures, according to Beer's law, and plotting the absorbance against concentration which given a straight line with a slope equals to ε for this complex. This was illustrated inTable (1): [24, 25].

Table 1: Molar absorptivity of complexes at four temperature

T(k)	*Molar absorptivity ε (L. $mol^{-1}cm^{-1}$) of ascorbic acid and Nickel*
293	3660
298	3773
303	4125
308	4276

The equilibrium constants calculated by this method were determined in four different temperatures (293,298,303,308) K as shown in Table (2)

Table 2: The equilibrium constants of acid -metal complex at different temperatures

T(k)	ΔG°(J.mol^{-1})	ΔH°(J.mol^{-1})	ΔS°(J.mol^{-1} K^{-1})
293	-38245.23	20618.72	200.900
298	--39170.41	20618.72	200.634
303	-40155.12	20618.72	200.573
308	-40817.7	20618.72	199.468

The results of table (2) show that these stability constants changes slightly with the range of temperature used in this work (293-308K). It increases with increase in temperature for (acid -metal) complex. That mean the stability of complex increase with temperature which means the bond between them becomes stronger [26, 27].

Thermodynamic Parameters: The free energy changes ΔG^{0}, the enthalpy changes $\Delta H^{0}$and the entropy changes ΔS^{0}, was calculated at four different temperatures (293,298,303,308) K for complex.

The enthalpy changes were calculated by substitute the value of the slope of the plot (*LnKeq*vs.*1/T*) in the vant Hoff equation (4), the result as shown in Figure (4) and Table (3) [28-30].

$$\ln Keq = -\Delta H^{o}/RT + \Delta S^{o}/R \quad .... (4)$$

Slope =$-\Delta H^{o}/R$

R = gas constant.

The change in Gibbs free energy can be determined from equation (5), the relation between K_{eq} and ΔG^{o} and the entropy changes from equation (6).

$$\Delta G^{o} = -RT\ Ln\ Keq \quad ... (5)$$

$$\Delta G^{o} = \Delta H^{o} - T\ \Delta S^{o} \quad ... (6)$$

Table 3: Thermodynamic parameters for ascorbic Acid-Nickel in deionized water at different temperature

Temp. (K)	K eq (L.mol^{-1}) of ascorbic acid and Nickel in water
293	6.67×10^{5}
298	7.38×10^{5}
303	8.38×10^{5}
308	10.9×10^{5}

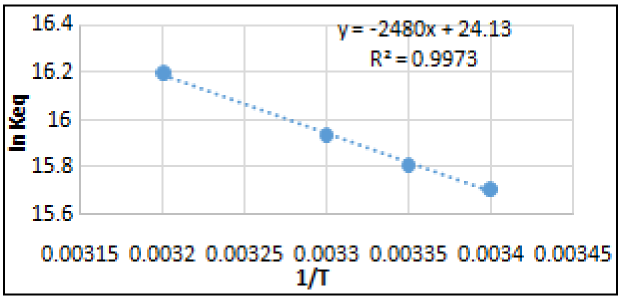


Figure 4: van' t Hoff plot for Ascorbic acid -Nickel in deionized water

The negative values of Gibbs free energy refer to spontaneous interaction between acid and metal ion, in direction of equilibrium and increase with increase in temperature. The positive values of entropy occur because water molecules that arranged around the acid and metal became more random because of hydrophobic interaction. The positive enthalpy and entropy refers to hydrophobic associated and electrostatic interaction [31].

Interaction Kinetics: In order to investigate the interaction kinetic of metal ion with acid the absorbance of complexes was collected with time at a certain wave length (261nm), temperature and its stoichiometric ratio. The first order rate equation (7) and the second order rate equation (8) were applied.

ln A = -kt + lnA_o…. (7) first order equation

(1/A) -(1/A_o) =Kt… (8) second order equation

A = absorbance at time t.

A_o= absorbance at time zero.

k = rate constant.

The complex will be stable in about (50-55 minute) which demonstrated from the constant absorbance. The application of the first and second order of the reaction was shown in Figure5. Table (4) illustrate second order rat constant for the complex of ascorbic acid-nickel

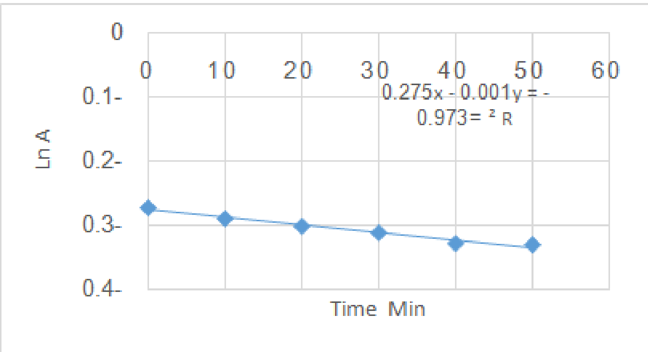


Figure 5 (a): The application of the first order reaction equation for complex ascorbic acid – nickel at 293K

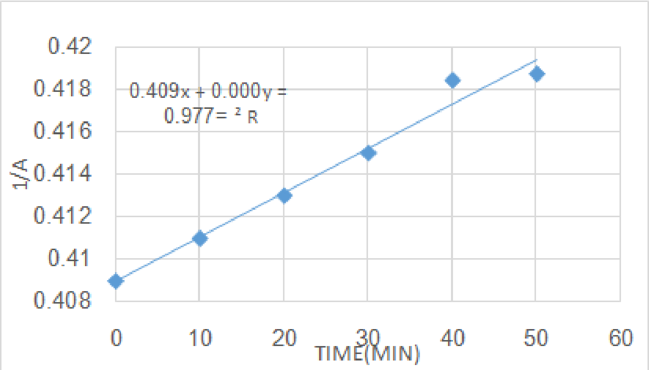


Figure 5 (b): The application of the second order reaction equation for complex ascorbic acid – nickel at 293K

The interaction between ascorbic acid-nickel is a second order with a rate constant $k=2\times10^{-3} min^{-1}M^{-1)}$

Table 4: The second order rate constants for ascorbic acid nickel complex

second order rate constant ($min^{-1}M^{-1}$) at 293(K)	second order rate constant ($min^{-1}M^{-1}$) at 298(K)	second order rate constant ($min^{-1}M^{-1}$) at 303(K)	Second order rate constant ($min^{-1}M^{-1}$) at 308(K)
2×10^{-3}	3.2×10^{-3}	4.3×10^{-3}	5.1×10^{-3}

The results from table 4 indicate that the rate constant increasing with increase temperature.

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