Study of Interaction between Vitamin C and Nickel (Π) Ion using a Polarographic Methods

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Abstract
The Polarographic study of the interaction between ascorbic acid and Ni^{+2} was carried out at dropping mercury electrode [DME] . This study included the determination of the kinetic parameters ($k°_{fh}$,αn) and thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of Ni^{+2} complexes with ascorbic acid in 0.1 M KCl solution over the temperature rang of (294-309)K. The electrode processes were irreversible and diffusion controlled.

Keywords : kinetic parameters, thermodynamic parameters,Ni^{+2} , Vitamin C complexes, Polarography

دراسة التآثر بين فيتامين سي و آيون النيكل الثنائي باستخدام طرق البولاروغرافي

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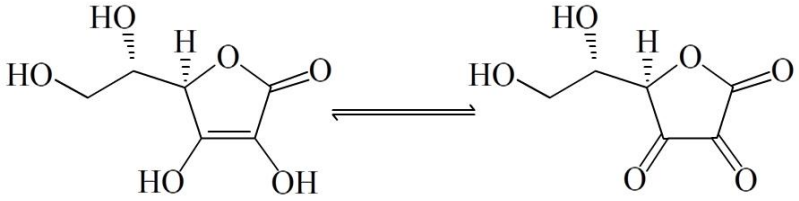
الخلاصة:
استخدمت تقنية البولاروغراف النبضي المشتق وبولاروغراف التيار المباشر لدر اسة التآثر بين ايون النيكل الثنائي وحامض الاسكوربيك باستخدام قطب الزئبق المتق اطر، واشتملت الدراسة تعيين الدوال الحركية (ثابت سرعة التآثر ومعامل الانتقال الكاثودي) وكذلك حساب الدوال الثرموديناميكية، الانثاليبي، وطاقة كيبز الحرة، والانتروبي لعملية التعقيد بين ايون النيكل وحامض الاسكوربيك في مدى من درجات الحرارة بين (294–309) كلفن وتبين ان عمليات القطب غير عكسية ومسيطر عليها بالانتشار.

Introduction:

Vitamin C, or ascorbic acid , is a vitamin that can be found in various fruits and vegetables. The reduced form of the vitamin is referred to as L-ascorbic acid (Figure 1) , and the oxidized form is referred to as dehydroascorbic acid. In humans, both forms are biologically active. The total vitamin C activity is the sum of both forms, [1]



L-ascorbic acid L-dehydroascorbic acid

Figure1- L-ascorbic acid molecule and L-dehydroascorbic acid

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Vitamin C plays a vital role in our lives; Firstly, it contributes in to the synthesis of collagen tissue around bones, teeth, cartilage, skin, and damaged tissue. Second, this vitamin is needed to activate various enzymes related to the nervous system, hormones, and detoxification of medicine and poison in the liver. Third, its role as an antioxidant is well-known in society; its solubility enables it to work as antioxidant within our bodily fluids. Fourth, Vitamin C increases the rate of absorption of iron, calcium, and folic acid. Fifth, it reduces allergic reactions, boosts the immune system, stimulates the formation of bile in the gallbladder, and facilitates the excretion of various steroids [2].

Ascorbic acid is one of the important water soluble vitamins and is easily absorbed but it is not stored in the body. Most plants and animals synthesize ascorbic acid for their own requirement. However, apes and humans cannot synthesize ascorbic acid due to lack of an enzyme gulonolactone oxidase. Hence, ascorbic acid has to be supplemented mainly through fruits, vegetables and tablets [3].The US recommended daily allowance for ascorbic acid ranges between 100–120 mg/ per day for adults. Many analytical methods have been reported in the literature for the determination of the ascorbic acid contents in different pharmaceutical products, fruits, vegetables and biological fluids [4-6].

Some elements may be micronutrient and are required in small amounts for normal healthy growth, Nickel is present in trace quantity in human body and plays important role in functioning of biological processes. [7] Nickel is a part of so many enzymes which are present in human. Due to such biological importance, it becomes essential to study its complexing tendency with therapeutic compounds. It has been proved that complexation of metals with drugs influences biological process that are metal dependent, Beside this, metal drug complex may be more effective than drug itself.[8]

In this work, we demonstrated the binding of Vitamin C and Ni(II) and the thermodynamics of their interaction. Kinetic parameter such as the formal rate constant and the transfer coefficient, thermodynamic parameters $\Delta H^{\#}_{P}$, $\Delta H^{\#}_{V}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, of Ni(II) complex with ascorbic acid in 0.1 M KCl solution were determined,and its temperature effect. In order to attain these objectives, we planned to carry out detailed investigation of Vitamin C and Ni(II) using Direct current Polarography and Differential pulse polarography .

Experimental :

Apparatus:

A Princeton Applied Research polarographic analyzer, model 174 (PAR 174) in conjunction with a model 170/70 drop timer , and an X-Y recorder model C 1924 from SIEMENS made in Germany, Kompensograph was used for the Polarographic measurements. A dropping mercury electrode was used as working electrode, and a saturated calomel electrode (SCE) as reference electrode. The auxiliary electrode was a mercury pool .

Reagents:

Pure deionized water was generated using an LV-08 Ultra pure water device. All the solutions were prepared from pure deionized water and analytical reagent grade chemicals (MERCK) for KCl and $Ni(NO_3)_2$.6H2O. L- ascorbic acid from (HIMEDIA), stock solution of ascorbic acid were prepared freshly every day and kept in the dark to minimize decomposition.

Procedure:

The general procedure for polarography is as follows :

A 30 ml of KCl (0.1) M was placed in a Polarographic cell as a supporting electrolyte and deoxygenated by passing nitrogen gas that was purified and equilibrated through bubbling in acidic Vanadium (II) solution [9] over (25g) heavily amalgamated zinc and thereafter through distilled water, for (10) minute.

1 ml of Ni (II) solution and 2 ml of L- ascorbic acid solution were added to the cell and deoxygenated again for (10) minute. The instrumental setting for Differential Plus Polarography (DPP) and Direct Current Polarography (DCP) was as follows :

Potential scan rate, 10 mv/s; drop life, 0.5 s; modulation amplitude 50 mv; and current range 0.1 mA.

Results and Discussion:

A well-defined two-electron reversible reduction and diffusion controlled wave of Ni (II) was observed in 0.1 M KCl solution. The half wave potential (peak potential) for Ni(II) was (- 1.05v) VS saturated calomel electrode (Figure 2) :

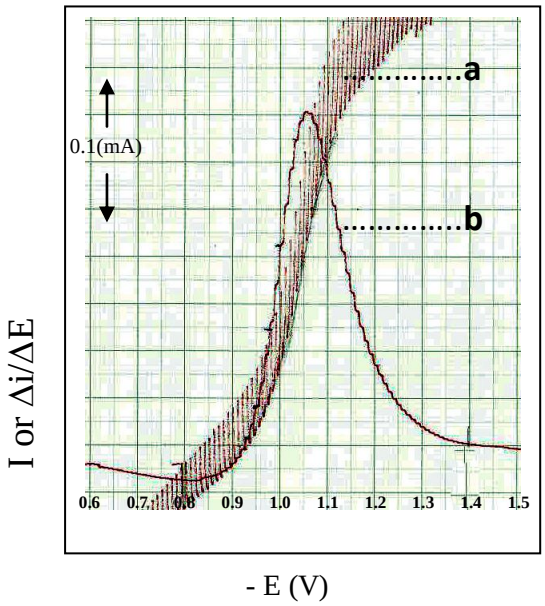

Figure 2-Polarogram of Ni(II) $6.2x10^{-5}$ M in 0.1 M KCl

Linear relationship between concentration and diffusion current (id) was obtained with the value of correlation coefficient (r^2) near to one, this has been proved statistically by applying straight line equation .(Figure 3 and 4).

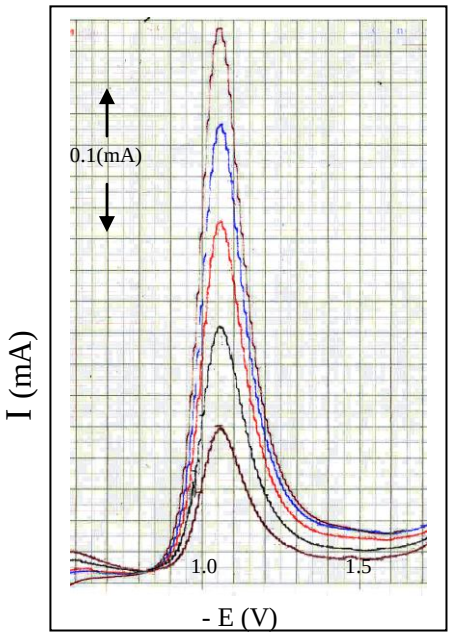

Figure 3- polarograms of different concentration of Ni(II) in 0.1 M

An increase in the wave hight (ip) of the ion signal was observed without any change in its $E_{1/2}$ value which understood in the light of Ilkovic equation (1), [10,11] :

$id=607nD^{1/2}m^{2/3}t^{1/6}C$ …….(1)

where *id* is diffusion current in (µA) , *n* is the number of electrons transferred in the reduction process, *D* is the diffusion coefficient of the depolarizer in (cm^2/sec) , *t* is the drop-time expressed in seconds , *C* is the depolarizer concentration given in (m.mol / liter) and *m* is the mass flow rate of Hg through the capillary (mg/sec).

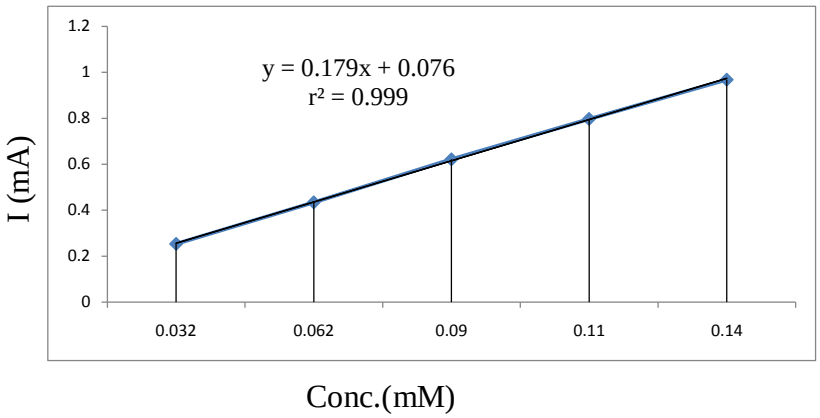

Figure 4- Correlation between concentration and peak current (id) of Ni(II) in 0.1 M KCl.

Ascorbic acid reduction on DME give one Polarographic wave with a peak potential (E ½) of (+0.03v) in (0.1) M KCl VS saturated calomel electrode. E ½ is independent of concentration. The limiting current id is controlled by diffusion and is proportional to the concentration of ascorbic acid, the electron transfer is not reversible process as no linearity is observed in the plot of E vs log i/id-i.
For each Polarographic measurement, the Heyrovsky –Ilkovic equation (2) was used to calculate the number of electron (n) required for the reduction [12]:

$$E = E_{1/2} - 0.059/n \times \log i/(id-i) \qquad \text{……..(2)}$$

Thus the value of n was obtained from the slop of the straight line corresponding to E d.c Vs log i/(id-i),figure(5).

The intercept of the same plot gives the value of E ½ , i the diffusion current and id the limiting diffusion current. The whole number value of n is taken as a sign of a reversible reduction [13,14] .

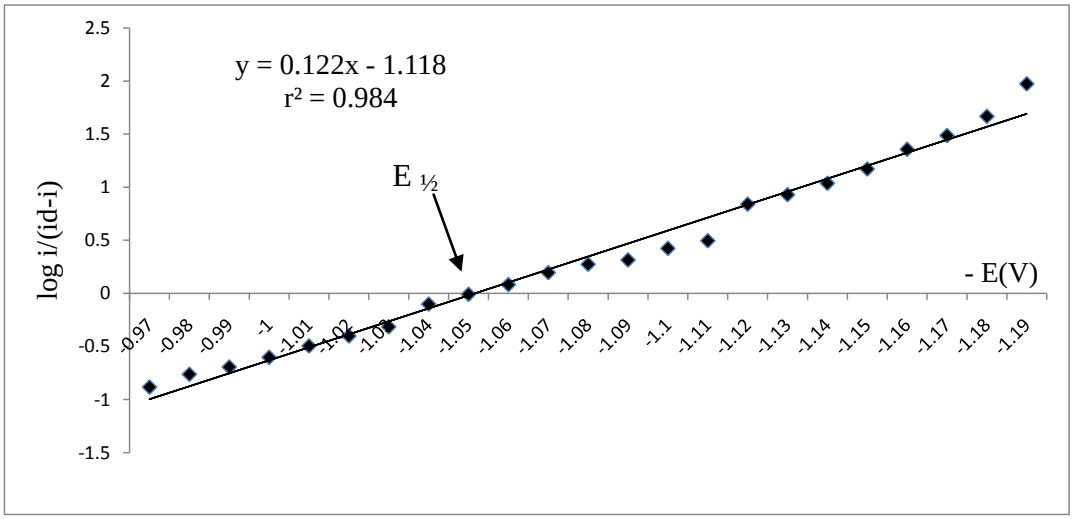

Figure 5 - Effect of E(V) on the variation of log i/(id-i) using Heyrovsky–Ilkovic plots for 6.2 x 10^{-5} M Ni(ΠI) reduction, n=slop/0.059=2.0

When a solution of ascorbic acid was added, the peak potential(Ep) of Ni(ΠI) unaffected and remains at -1.05V, Whereas, The diffusion current were found to decrease with increase in ligand concentration (A.A) and the appearance of a new peak in a more negative potential (-1.63) which suggests the complex formation, and increasing the activation energy involved in reduction [15].The complex ion formed is of a greater size as compared to the aqua metal ion hence there is a low value of diffusion current with the increase of ligand concentration[16].(Table 1 & Figure 6).

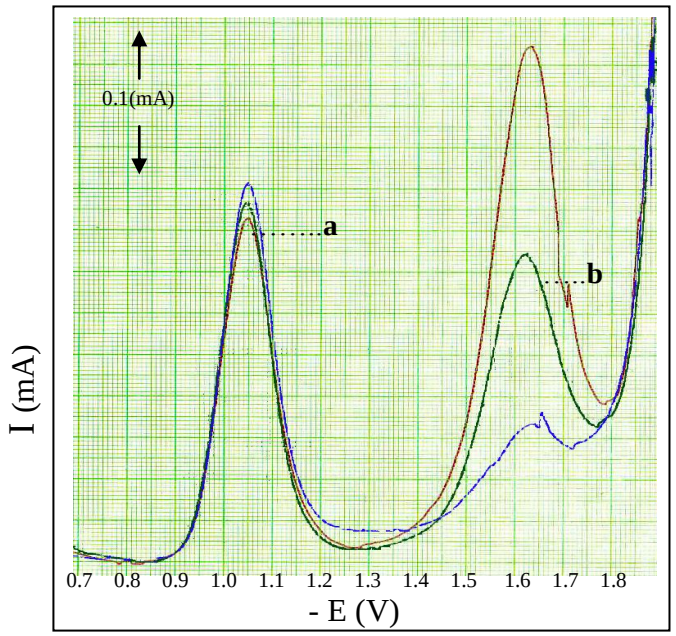

Figure 6- Polarogram of Ni(Π) – ascorbic acid system in 0.1M KCl.
a- Ip for Ni(Π) . **b-**Ip for (Ni(Π) – AA) complex

Table 1- Electrochemical reduction of Ni(Π) – ascorbic acid system in 0.1M KCl at DME and various concentration.

S.No	Ni(II) conc. (M)	Ascorbic acid Conc. (M)	Ip Ni(II) (mA)	Ep Ni(II) (mV)	Ip Ni(Π) –AA complex (mA)	Ep complex (mV)
1	$3.2x10^{-5}$	----------	0.055	-1.05	----------	----------
2	$3.12x10^{-5}$	$3.12x10^{-5}$	0.050	-1.05	0.0088	-1.63
3	$3.03x10^{-5}$	$6.06x10^{-5}$	0.047	-1.05	0.0396	-1.63
4	$2.94 x10^{-5}$	$8.80x10^{-5}$	0.045	-1.05	0.0671	-1.63

The variation of current and potential of Ni(II) –ascorbic acid complex as function of temperature and concentration were measured by D.C. and D.P. polarography .
The nature of the current-voltage curve of Ni(II) –ascorbic acid complex was irreversible, As the ascorbic acid concentration increase the irreversibility of the electrode reaction increase.

Kinetic parameters:

Kinetic parameters (K^0_{fh}, αn) were calculated by Meites & Israel's method[17] and Gaur & Bhargava's method.[18]
Meites – Israel modification of Kotecky's method, equation (3,4):

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n} \log \frac{i}{(id - i)} \quad \text{.....(3)}$$

$$E_{1/2} = \frac{0.0591}{\alpha n} \log \frac{1.349\ K^0_{fh} t^{1/2}}{D^{1/2}} \quad \text{.....(4)}$$

Gaur & Bhargava's modification ,equation (5,6):

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{\alpha n} \log \frac{i}{(id - i)} \quad \text{.....(5)}$$

$$E_{1/2} = \frac{0.0591}{\alpha n} \log \frac{K^0_{fh} t^{1/2}}{(\text{antilog } C)\ D^{1/2}} \quad \text{.....(6)}$$

Where
K^{o}_{fh} = formal rate constant for forward reaction
D = diffusion coefficient
αn = transfer coefficient
$E_{d.e.}$ and $E_{½}$ were determined with respect to calomel electrode. The values of αn were obtained by equation-3 (Meites – Israel method) and equation-5 (Gaur-Bhargava method). The values of K^{o}_{fh} were determined by equation-4 (Meites – Israel method) and equation-6 (Gaur-Bhargava method). The values of diffusion coefficient (D) were determined by using Ilkovic equation-1.

Temperature effect:

A gradual change in diffusion current and peak potential was observed when the solution temperature was increased from 294k to 309k , table-2. The potential peak becomes more positive with increase in temperature. The value of αn decrease with increase in temperature which implies that transfer of electrons becomes difficult [19]. Further the values of K^{0}_{fh} increases with increase in temperature which suggests that irrereversibility decrease, this implies that the reduction products are less stable at higher temperature.

Table 2 - Electrochemical reduction of Ni(II) – ascorbic acid system in 0.1M KCl at various temperature.

S. No	Ni (II) (M)	Vc (M)	T (k)	$E_{1/2}$	Idx100 (nA)	$D^{0.5}$ (cm^2/s)	αn ME (v)	αn GB (v)	$k°_{fh}$ ME (cm/s)	$k°_{fh}$ GB (cm/s)
1	3.2 X 10^{-5}	000	294	-1.05	0.95	2.83	2	2	2.95 x 10^{-35}	3.98 x 10^{-35}
2	3.03 x 10^{-5}	6.06 x 10^{-5}	294	-1.05	0.88	2.48	0.59	0.64	8.1 x 10^{-11}	1.4x 10^{-11}
3	3.03 x 10^{-5}	6.06 x 10^{-5}	299	-1.045	0.93	2.64	0.54	0.58	7.2 x 10^{-10}	1.6 x 10^{-10}
4	3.03 x 10^{-5}	6.06 x 10^{-5}	304	-1.04	0.99	2.79	0.48	0.53	1.02 x 10^{-8}	1.69 x 10^{-9}
5	3.03 x 10^{-5}	6.06 x 10^{-5}	309	-1.03	1.1	3.4	0.43	0.47	1.09 x 10^{-7}	2.7 x 10^{-8}

Thermodynamic parameters:

Thermodynamic parameters ($\Delta H^{\#}_{P}$,$\Delta H^{\#}_{V}$,$\Delta G^{\#}$,$\Delta S^{\#}$) have been reported in table-3. These parameters are imported to interpret the binding mode of metal-ligand complex[20]. The enthalpy of activation at constant pressure ($\Delta H^{\#}_{P}$) has been calculated by substituting the value of slope of the plot (log k^{0}_{fh} vs 1/T) in the Vant Hoff equation [20,21]:

$\Delta H^{\#}_{p}$= 2.303R × Slope .

Where R= Gas constant, the value of slope comes out to be -19139 ($cm.s^{-1}.K$), figure-7:

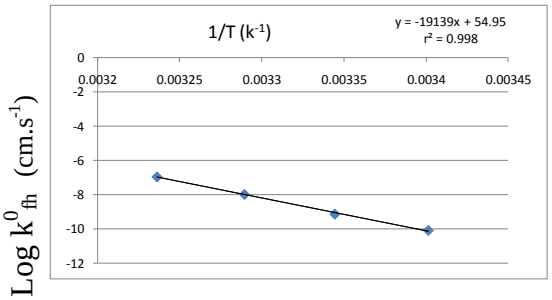

Figure7– Log k^{0}_{fh} against 1/*T*

The enthalpy of activation at constant volume was evaluated from this relation :
$\Delta H^{\#}_{p} = \Delta H^{\#}_{v} + RT$
The activation free energy change ($\Delta G^{\#}$) was determined by relationship:
$K^{0}_{fh} = (kT/h)\, r_o \exp\text{^-}\Delta G^{\#}/RT$
Where , k = Boltzmann constant, h = Plank's constant, r_0 = mean distance between depolarized ions in the bulk solution, r_0 is taken as 2 X 10^{-8} cm.[22], R = Gas constant, T = absolute temperature.
The results summary in table-3.

Table 3 - Thermodynamic parameters at different temperature.

S.No	T (K)	$\Delta H^{\#}_{p}$ J.mol^{-1}	$\Delta H^{\#}_{v}$ J.mol^{-1}	$\Delta G^{\#}$ J.mol^{-1}	$\Delta S^{\#}$ J.K^{-1}
1	294	366457.1	364012.8	85428.2	947.6
2	299		363971.3	81534.2	944.6
3	304		363929.7	76074.7	946.9
4	309		363888.1	71418.2	954.8

The entropy of activation ($\Delta S^{\#}$) was calculated using following equation; $\Delta S^{\#} = (\Delta H^{\#}_{v} - \Delta G^{\#})/T$
Thermodynamic parameters presented in (Table 3) shows that the activation free energy is positive suggesting the non spontaneous nature of the electrode process.
In positive value of $\Delta S^{\#}$ and $\Delta H^{\#}$ indicates that the process becomes spontaneous at high temperature, also the positive value of $\Delta S^{\#}$ and $\Delta H^{\#}$ refers to the types of interaction which are electrostatic in nature.

Conclusion:

It is clear from the study that the presence of a new peak in the more negative potential and a decrease in the current peak confirms the complex formation between Ni^{+2} and ascorbic acid, $E_{1/2}$ of Ni^{+2} peak shifts to more negative value with increase in ascorbic acid concentration. By employing the polarographic technique in 0.1 M KCl at 294 K to 309, the thermodynamic parameters ($\Delta H^{\#}$,$\Delta G^{\#}$,$\Delta S^{\#}$) were determined which suggests the non-spontaneity of the electrode reduction. Kinetic parameters (K^{0}_{fh} , αn) were calculated at different temperature, the formal rate constant for the forward reaction increase with temperature and αn decrease with temperature.

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