

Electrochemical Study of the Complexation of Quercetin with Lead (II) ion in acidic media

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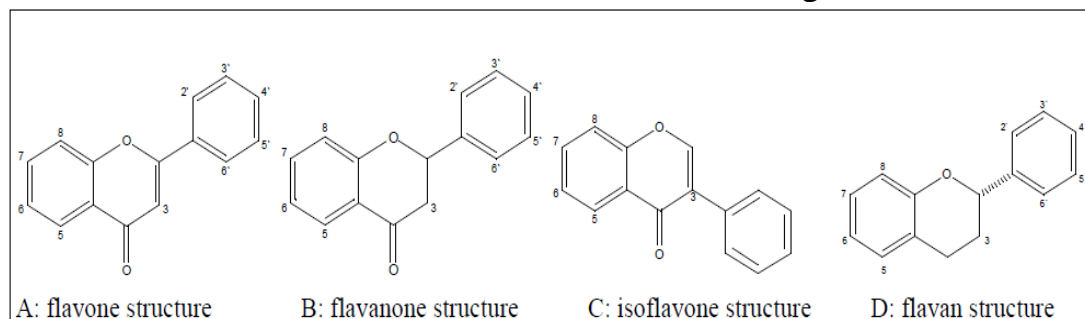
Abstract

Dietary flavonoids (poly phenols) are important phytonutrient component widely distributed in plant foods, flavonoids have beneficial biological activities, such as antioxidant activity, flavonoids can chelate with metal ions, the interaction of lead(II) ion with a poly hydroxylated flavonoids, the quercetin molecule, were investigated electrochemically in acidic media. The Differential Puls Polarographic Technique was used to determine the kinetics parameters (K^0 , f, h , αn) using Meites- Israel method, also thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG), entropy change (ΔS) of Pb^{+2} - complexes with Quercetin at (293- 313k). The ($K^0, f, h, \alpha n$) values for the kinetics of the electrode processes show that the electrode processes were irreversible and diffusion controlled.

Keyword, Quercetin, Pb^{+2} - Quercetin complexes, polarography, kinetics parameters, thermodynamic parameters.

Introduction

Flavonoids are a class of polyphenolic compounds which were presented in most plants, synthesized by the phenyl propanoid pathway, more than 6000 different flavonoids have been identified making them the largest group of plant chemicals, classified as flavones, flavonols, flavanones, flavanols, and isoflavones^(1,2), [figure-1].



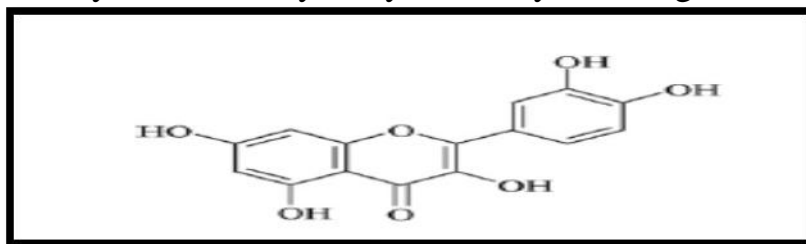
Figure(1) The general structure of flavonoids.

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In recent years ,flavonoids were found to have particular biological activities and therefore have gained increasing attention .previous studies showed that flavonoids have antibacterial, antioxidizing^(3,4), and anti-inflammatory activities^[5], as well as functions for prophylaxis of cancer and cardiovascular diseases^[6-10].

The pharmacological effects are related to the antioxidant activity of flavonoids ,arising through their ability to scavenge free radicals , when generated in excess ,free radicals can damage biomolecules ,and are therefore implicated in the etiology of several disease and ageing⁽¹¹⁾.

Quercetin (3,3',4,5,7-penta hydroxy flavone) is one of the most common flavonols present in nature that has attracted the attention of many researchers because of its biological properties⁽¹²⁻¹³⁾. Quercetin possesses three possible structural groups determinants for its free radical scavenging or antioxidant potential; the 3,4- dihydroxy (catechol) ,the 3-hydroxy-carbonyl and the 5-hydroxy -carbonyl⁽¹⁴⁾ , [figure -2].



Figure(2) The molecular structure of Quercetin.

This highly functionalized structure provides the possibility for a metal cation to interact with the substrate on the three complexation sites⁽¹⁵⁾. some elements may be micronutrients for many living organisms and are required in small amounts for normal healthy growth , but any metal ion in large amount will always cause acute or chronic toxicity^[16].

Lead is such a metal which is used in every thing from construction materials to batteries , alloys , textiles , dyes ,plumbing , fuel additives, ammuniton etc , Lead compounds are considered to be toxic pollutants.It may enter the human body through air , food , water or absorption through skin , with increase in concentration it can cause serious health problems [17,18].

The objective of the present work are , to determine the complexation of quercetin with lead (II) ion by the differential pulse voltammetry using a hanging mercury drop electrode ,(HMDE) , and the thermodynamics of their complexation, stability constant in 1 M HCl , kinetics parameter (K^o , α) and thermodynamic parameters (ΔH^o , ΔH^o_v , ΔS^o , ΔG^o) were determined in different temperature.

Experimental

Reagents

All the solutions were prepared and diluted with deionized water . Quercetin was from sigma aldrige –comp.Ltd., a stock solution was prepared by the use of absolute ethanol as a solvent supplied from Scharlau comp. . Lead nitrate from hemidia-comp.Ltd., Hydrochloric acid from BDH , sodium hydroxide and potassium chloride supplied from GCC-England , have been used as supporting electrolyte in adifferent concentrations.

Procedure

The general procedure for apolarographic measurements was as follows :

A 15 ml of the experimental solution accurately measured and placed in a polarographic cell and deoxygenated with pre-purified nitrogen for 5 minutes , and performed under a nitrogen atmosphere .

Polarographic experiments were carried out with a par model 797Va poarographic analyzer equipped version 1.2.

The current voltage curves were measured manually and performed with three electrode system , a medium size hanging mercuric drop electrode as working electrode , platinum electrode as counter electrode and Ag/AgCl (in saturated 3M KCl) as a reference electrode .

The operating parameters were , Puls amplitude 50 mv, Puls time 0.02 sec , Scan rate 15mv/s, Initial potential (-1.0v) , End potential (1.0v) , Drop size 9mm³ , Voltage step 0.006v , Voltage step time 0.4 sec, Deposition time60sec,Equilibrium time 5sec.

Results and Discussion

Supporting electrolyte

The good of the preliminary studies is the choice of a supporting electrolyte which is made such that investigated compound is stable for at least 30Min., and yields awell-developed wave separated from waves of other components present in the sample and well separated from the current of the supporting electrolyte together with the range of potentials in which the electrolysis occurs .

Avariety of supporting electrolytes can be used in determination of organic compounds . These are usually buffers or solutions of strong acids or strong bases , the concentrations of them is kept at least 20 times higher than concentration of the electroactive species ^[19].

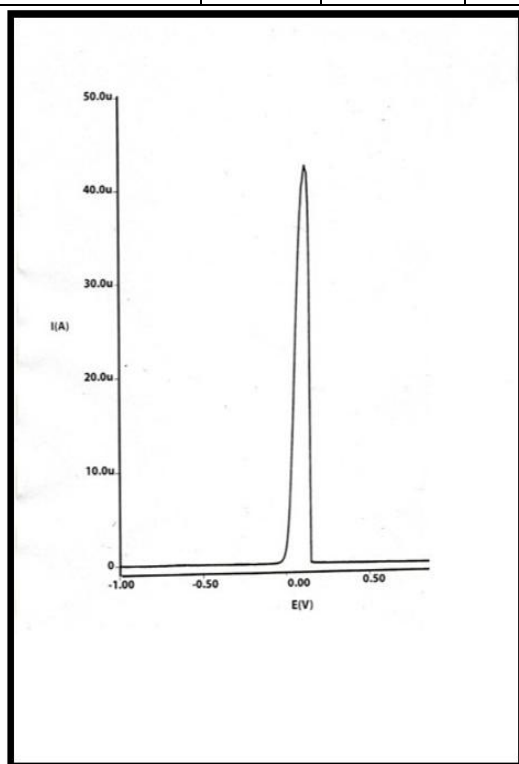
The polarographic measurements for Quercetin[Que] in several supporting electrolytes such as KCl, HCl , and NaOH were performed . It was found that HCl was the most suitable supporting electrolyte . The

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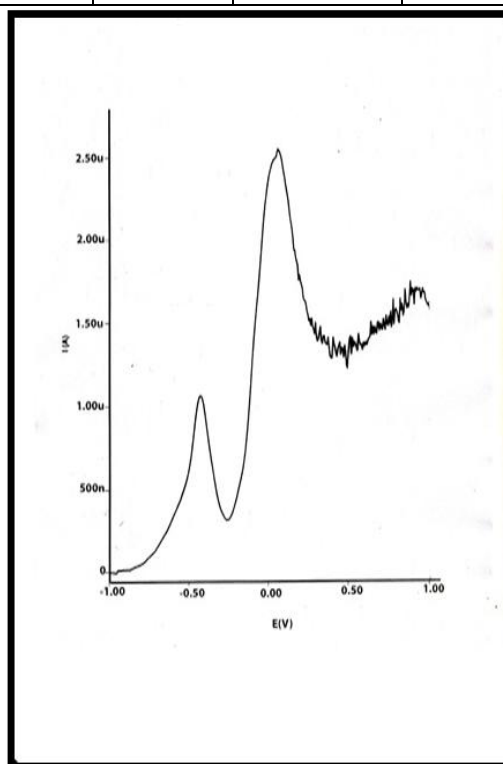
results obtained are summarized in Table -1, and the differential puls polarograms are shown in figures (3a-c).

Table(1): Peak potential and peak current of 1.2×10^{-4} M Quercetin in different supporting electrolyte.

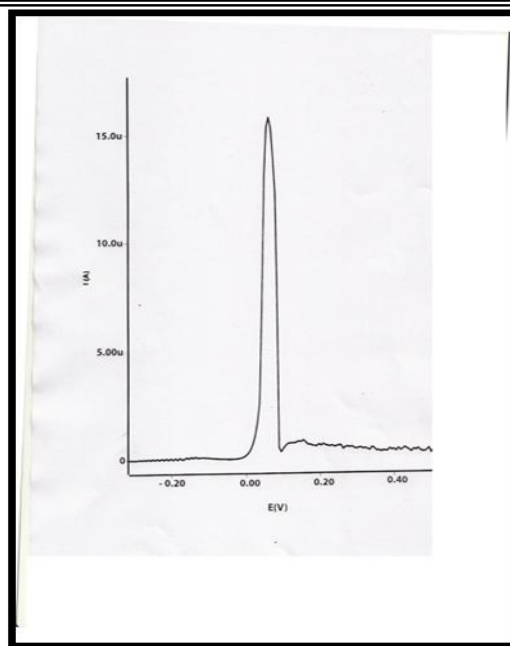
Concentration of supporting electrolyte	Potassium chloride		Sodium hydroxide		Hydrochloric acid	
	Ep(v)	Id(uA)	Ep(V)	Id(uA)	Ep(V)	Id(uA)
1M	0.137	16.40	0.0594 - 0.429	2.55 1.03	0.0832	44.10
0.1M	0.125	23.50	-0.0061 0.291	5.82 0.464	0.0715	42.90
0.01M	0.119	26.60	0.0891 0.428 -0.173	2.74 0.404 0.106	0.0715	41.50



- 3a-



-3b-



-3c-

Figure (3)- Differential Pulse Polarogram of 1.2×10^{-4} M Quercetin in a-1M HCl , b- 1M NaOH , c- 1M KCl

Polarographic wave of Lead (II)ion and Quercetin

A well defined two- electron reversible reduction and diffusion controlled wave of Pb^{+2} was observed in 1M HCl solution , the half wave potential or peak potential (E_p) for Pb^{+2} was ($- 0.387V$) VS. Ag/AgCl electrode , Figure(4).

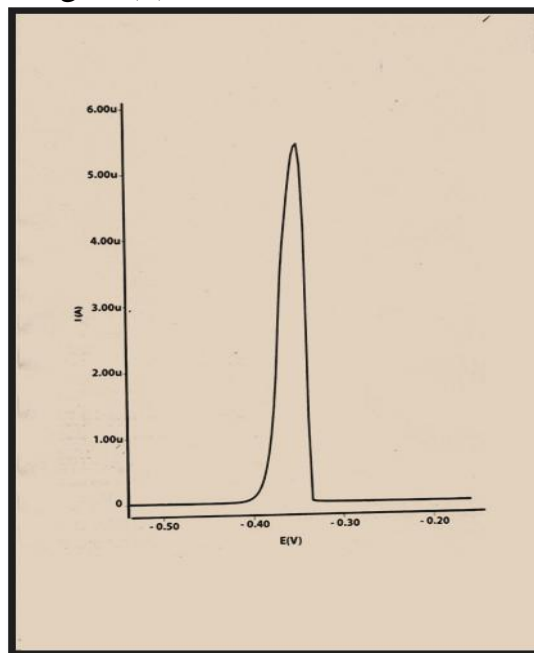


Figure (4) DPP of 1×10^{-4} M Pb^{+2} ion in 1M HCl.

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Quercetin reduction at hanging mercury drop electrode (HMDE) gave one polarographic wave with a peak potential of (+ 0.0832V) in 1M HCl VS. Ag/AgCl electrode , (Ep) is independent of concentration . The limiting current (id) is controlled by diffusion and is proportional to the concentration of Quercetin .

An increase in the wave height (Id) with the increase in concentration which understood from Ilkovic equation (1) [20] .

$$I_d = 706 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6} \cdot C \dots\dots\dots(1)$$

Where

Id is the average diffusion current in microampere during the live of the drop, n is the number of electrons consumed in the reductive of one molecule of the electroactive species , D is the diffusion coefficient of the reducible or oxidisable substance expressed as cm²/sec. ,m is the rate of flow of mercury from the dropping electrode expressed in mg/sec., t is the drop time in sec. , and C is the concentration in mmole/L .,the constant 706 is a combination of natural constants .

Linear relation between concentration and diffusion current (Id) was obtained with the value of correlation coefficient (r²) near to one , this has been proved statistically by applying straight line equation , Figure(5).

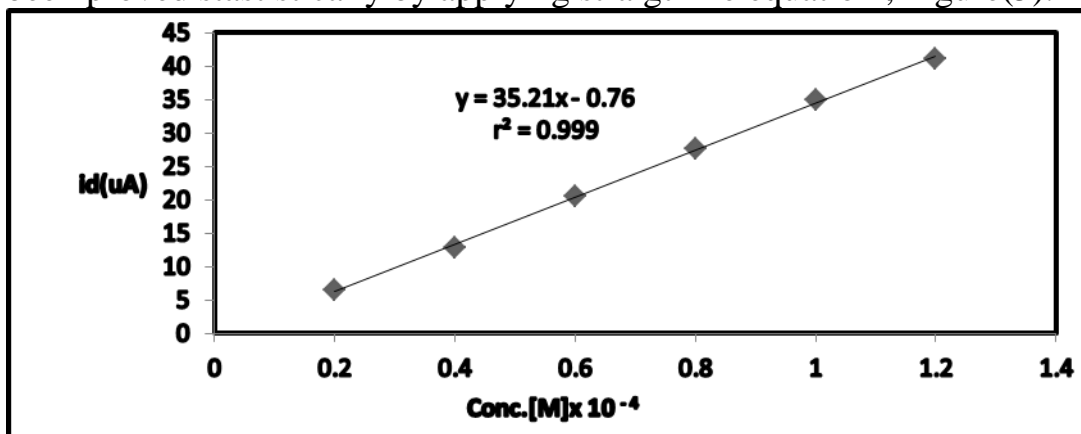


Figure (5) – Relation between concentration and Peak current of Quercetin at 298K.

The electron transfer is a reversible process as a linearity is observed in the plot (E) vs. log (i/id – i) , for each polarographic measurement the Heyrovsky – Ilkovic equation (2) [21] , Was used to calculate the number of electron (n) required for the reduction .

$$E = E_{1/2} - 0.0591 / n \cdot \log i/id - i \dots\dots\dots(2)$$

Thus the value of (n) was obtained from the slope of the straight line corresponding to (E) vs. log i/id– i .The whole number value of (n) is taken as a sign of reversible reduction , Figures (6 and 7).

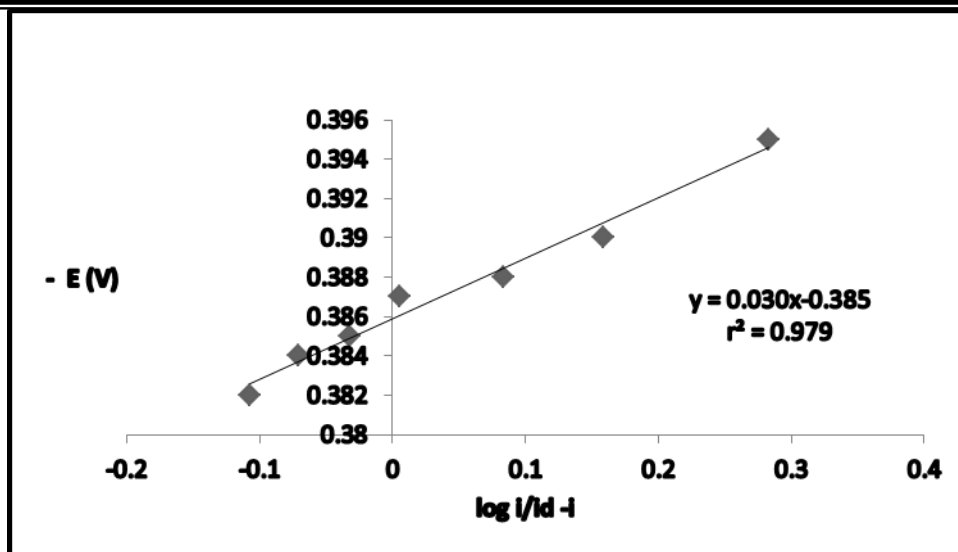
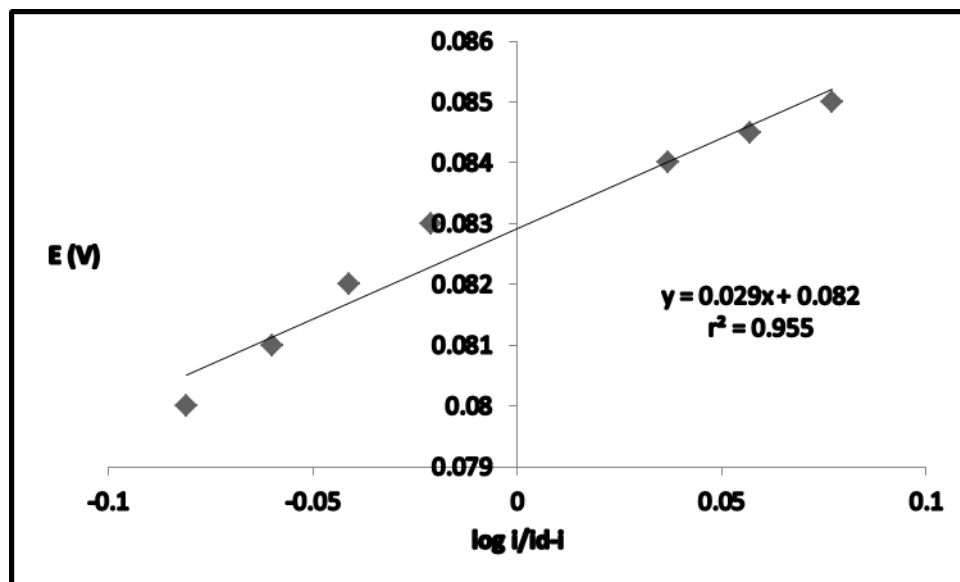


Figure (6): Heyrovsky – Ilkovic plots for 1×10^{-4} M Pb(II) reduction.



Figure(7) : Heyrovsky – Ilkovic plots of 1.2×10^{-4} M Quercetin.

Quercetin – Pb⁺² complexation

A ddition of a different concentration of Quercetin in a range of $2 \times 10^{-5} - 1 \times 10^{-4}$ M to a solution of a constant concentration 1×10^{-4} M of Pb⁺² ion , show the appearance of a new peak in a more negative potential (- 0.446v) than the Pb (II) peak with a gradual decrease in a peak current of Pb(II) ions which suggests the complex formation between them, Figure(8).

The peak potential of the complex formed shifts cathodically with the increase in ligand concentration due to increasing the activation energy involved in reduction^[22] .

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Stoichiometry and stability constant

The stoichiometry and the stability constant of lead (II) complex with Quercetin using a polarographic method were calculated by lingane equation (3) [23].

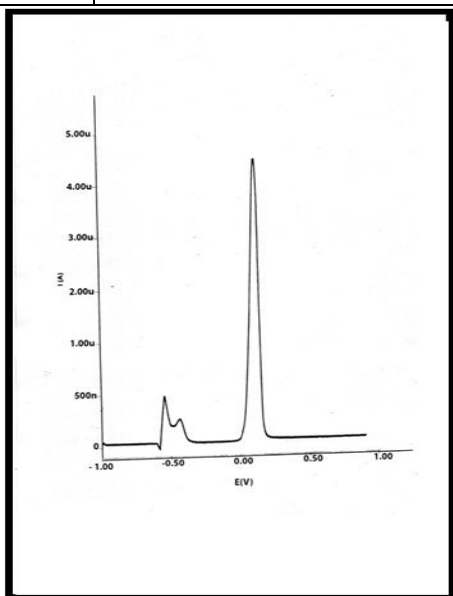
$$\Delta E_{1/2} = (E_{1/2})_C - (E_{1/2})_M = - (0.0591/n) \log K_{ML} - (0.0591/n) \cdot P \cdot \log [L] \dots [3]$$

This method is based on the observation that the complexation of a metal by a ligand will cause a shift towards more negative potentials in the polarographic reduction wave of the metal ion, the magnitude of the shift is directly related to the thermodynamic stability of the complex and the concentration of the complexing ligand.

A straight line was obtained by the application of lingane equation(3), as shown in Figure (9) and Table (2). The slope of line allows the determination of the coordination number P, P=1, which implies that the stoichiometric ratio of Pb(II) – Quercetin complex is 1:1, and the stability constant were determined from the intercept, $\log k_{ML} = 7.7$.

Table(2): Application of lingane equation in pb-Quercetin complex at 298K, and 1×10^{-4} M Pb (II) ion.

NO.	Conc. of [L], M	Log [L]	$\Delta E_{1/2}$, (V)
1	2×10^{-5}	-4.69	-0.031
2	4×10^{-5}	-4.39	-0.040
3	6×10^{-5}	-4.22	-0.052
4	8×10^{-5}	-4.09	-0.056
5	1×10^{-4}	-4.00	-0.059



Figure(8): Differential pulse Polarogram of Quercetin-Pb(II) System in 1M HCl.

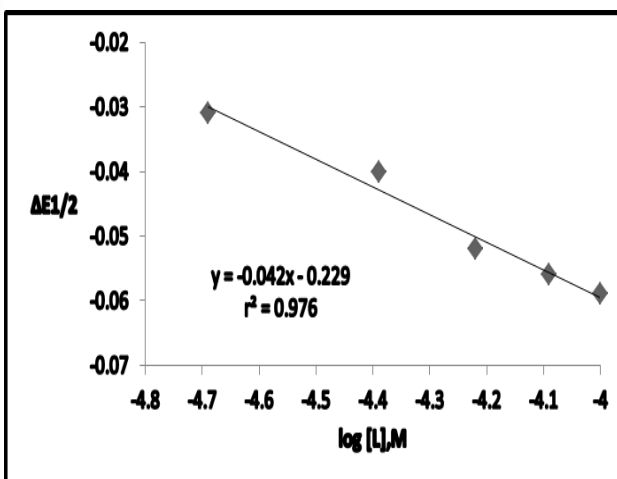


Figure (9): Lingane plot of $\Delta E_{1/2}$ of Pb-

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Kinetic parameters

kinetic parameters ($K^{0}_{fh,\alpha n}$) were calculated by Meites & Israel s method⁽²⁴⁾:-

$$E_{d.e} = E_{1/2} - 0.0542/\alpha n \cdot \log i/id - i \dots\dots\dots(4)$$

$$E_{1/2} = 0.0591/\alpha n \cdot \log 1.349 K^{0}_{fh} \cdot t^{1/2} / D^{1/2} \dots\dots\dots(5)$$

Where

K^{0}_{fh} = formal rate constant for forward reaction

D= Diffusion coefficient

αn =transfer coefficient

$E_{d.e}$ and $E_{1/2}$ were determined with respect to Ag/AgCl electrode , the values of αn were obtained by equation (4) . and K^{0}_{fh} by equation(5), and The value of diffusion coefficient (D) were determined by using Ilkovic equation(1).

Temperature effect

The effect of temperature on a reduction of Pb(II)-Quercetin[1:1] were listed in table (3), temperature has a very little effect on peak potential (E_p) but (i_d) increase with the temperature of about 1.2% , further the values of (K^{0}_{fh}) decrease with increase in temperature which suggests that irreversibility increase with increase in temperature , this implies that the reduction products are more stable at high temperature.

Thermodynamic parameters

Thermodynamic parameters (ΔH^*_p , ΔH^*_v , ΔG^* , ΔS^*) have been reported in table (4) .

These parameters are important to interpret the binding mode of metal-ligand complex^[25] .

The enthalpy of activation at constant pressure (ΔH^*_p) has been calculated by substituting the value of slope of the plot [$\log K^{0}_{fh}$ VS. $1/T$] in the van't Hoff equation^[26] , figure (10).

$$\Delta H^*_p = 2.303R \times \text{Slope}$$

R= gas constant

The enthalpy of activation at constant volume was evaluated from relation (6) and the activation free energy change (ΔG^*) was determined by relation (7) :

$$\Delta H^*_p = \Delta H^*_v + RT \dots\dots\dots(6)$$

$$K^{0}_{fh} = (k T / h) \cdot r_o \cdot \text{Exp} (- \Delta G^* / R T) \dots\dots\dots(7)$$

Where k= Boltzmann constant

h= plank's constant

r_o = mean distance between depolarized ions in the bulk solution , in general value of (r_o) is taken as 2×10^{-8} Cm .

R = gas constant

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T = Absolute temperature

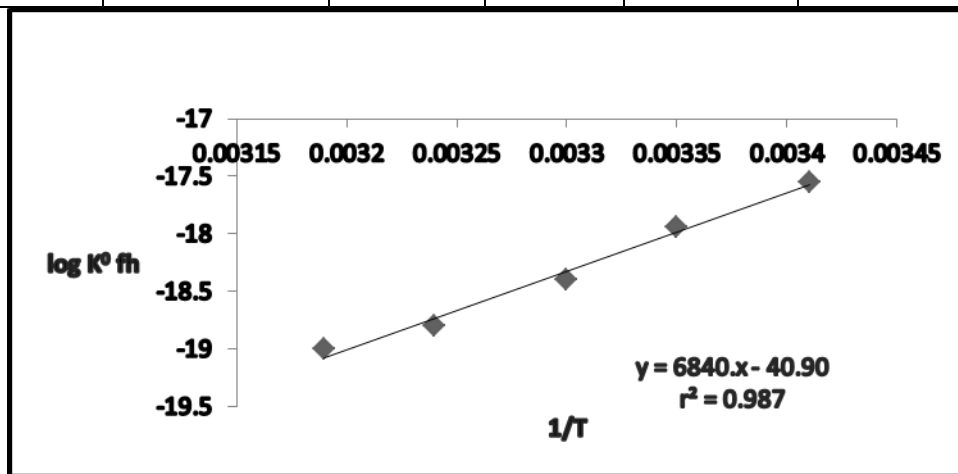
The entropy of activation (ΔS^*) was calculated using following equation

$$\Delta S^* = (\Delta H^*_{\nu} - \Delta G^*) / T \dots \dots \dots (8)$$

Table (4) show that the activation free energy ΔG^* is positive at all the temperature suggests the non spontaneous nature of electrode process ,and increase with increase in temperature. Positive value of ΔS^* suggests that formation of activated state is accompined by increase in entropy . This increase gradually decrease with increase in temperature. The positive value of ΔS^* and ΔH^* refers to the type of interaction between the metal and ligand which are electrostatic in nature.

Table(3)Electrochemical Reduction of[1:1] Pb⁺²- Quercetin system at HDME in 1M HCl at various temperatures.

T(K)	(Ep)C (V)	id(uA)	an	D ^{1/2} (Cm ² /S)	K ⁰ fh(Cm/s)
293	- 0.513	0.448	1.9718	1.139	2.805x 10 ⁻¹⁸
298	-0.524	0.455	1.9770	1.157	1.137x10 ⁻¹⁸
303	-0.539	0.509	1.9777	1.295	3.953x 10 ⁻¹⁹
308	-0.551	0.512	1.9779	1.302	1.570x10 ⁻¹⁹
313	-0.557	0.517	1.9780	1.315	9.954x10 ⁻²⁰



fig(10): logk⁰ fh against 1/T.

Table(4)Thermodynamic parameters at different temperature.

T(K)	ΔH^*_p (J/mole)	ΔH^*_ν (J/mole)	ΔG^* (J/mole)	ΔS^* (J/K)
293	130966	128503	15433	386
298	130966	128488	15980	378
303	130966	128447	16575	369
308	130966	128405	17156	361
313	130966	128364	17551	354

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Conclusion :

The result obtained prove that hydrochloric acid was the most suitable supporting electrolyte for the reduction of Quercetin by a differential puls polarography ,the presesnce of a new peak in the more negative potential and a decrease in the current peak confirms the complex formation between lead(II) and Quercetin with a stoichiometry of [1:1] , and stability constant $\log k = 7.7$. The thermodynamic parameters (ΔH^*_{p} , ΔH^*_{v} , ΔG^* , ΔS^*) were determined at different temperature ,which suggests the non- spontaneous of the electrode reduction.

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دراسة كهروكيميائية لتعقيد أيون الرصاص الثنائي مع الكيورستين في الوسط الحامضي

نجدت رضا الخفاجي

الهام مجيد الرفيعي

جامعة بغداد- كلية العلوم - قسم الكيمياء

بغداد- الجادرية

الخلاصة

تعد مرتبطات الفلافونيد من المركبات متعددة الفينولات ذات المنشأ الغذائي , وهي موجودة بكثرة في النباتات , ولها استخدامات طبية واسعة بسبب فعاليتها كمواد مضادة للاكسدة , ولقدرتها على الارتباط مع أيونات الفلزات , في هذا العمل تم إجراء دراسة كهروكيميائية لارتباط أيون الرصاص الثنائي مع أحد مرتبطات الفلافونيد , الكيورستين في الوسط الحامضي حيث تم استخدام تقنية البولاروغراف النبضي المشتق لغرض تعيين المتغيرات الحركية ($K^{\circ}fh,\alpha n$) بطريقة Meites- Israel , كذلك حساب الدوال الترموداينميكية , الانتالبي , طاقة جيبس الحرة , والانتروبي لعملية التعقيد في مدى من درجات الحرارة (293- 313) كلفن , ومن حساب ($K^{\circ}fh,\alpha n$) لحركيات القطب تبين أن عمليات القطب غير عكسية ومسيطر عليها بالانتشار .