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Theoretical, Voltammetric and Thermodynamic study for Cadmium(II)-Tyrosine Complex at 293-313 K

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Abstract

The electrochemical properties of the complexation was applied to evaluate different thermodynamic parameters (ΔG, ΔH and ΔS) for the cadmium (II)-tyrosine compound using voltammetric technique. The measurements have been investigated by square wave voltammetry using three electrode system consists of solid (platinum as working and auxiliary electrode) and Ag/AgCl immersed in saturated KCl as a reference electrode using to phosphate buffer solution (pH=7) at the range of temperatures (293-313K). Cadmium has a reduction peak potential at (-0.760 V) which is decrease gradually with an increasing of tyrosine concentrations added. Hartree-Fock calculations at basis set (STO-3G) were applied to evaluate the physic-chemical properties like bond length, bond angle, torsion and the thermodynamic parameters.

Key Words: square wave voltammetry, computational chemistry, complexation, thermodynamic

1. Introduction

Cadmium can be known as one of the heavy metal in the periodic table. This metal was found in many process in our life. Many factories were release this metal by platting, molding, dye manufactories, …etc. For this reason cadmium categorize as toxic for the body if accumulation[1]. The metals were consider as dangerous for the humans when they attached with active groups in the human body containing (-N and -OH) or with (proteins)[2].
The computational chemistry were used widely for prediction of COVID-19[3] and pKa[4], studying the substituents effect[5], lipophilicity[6,7], ionization potential[8] and rate constant[9].

The electrochemical method especially square wave voltammetry was used previously to study the interaction of complexation between many of metals like Co(II), Cd(II), Hg(II), Ti(III), Rh(III) and Rb(I) with the methyl yellow[10]. Some ligands have been prepared and characterized using conductivity and FTIR. The thermodynamic parameters were calculated for Schiff base as ligand with Cd^{+2}, Cu^{+2}, Ni^{+2}, Hg^{+2}…,etc[11].

The complexation between the amino acid (tyrosine) with metal have been determined using the (UV) technique[12]. While, the complexation of the cadmium (II) with pyridine derivative has been characterized in different solvents and binary solvents at a range of temperatures (298-318K) using the conducting technique[13].
The theoretical calculations shows that the complex for metals have been demonstrate with the ion pair at the nitrogen or oxygen atom in the compounds. The complexation was found with Cr(II), Co(II), Ni(II), Cu(II), Cd(II), …etc[14-16]. While pd(II), Zn(II) and Ni(II) have been studied their complexation with Sciff Base derivatives theoretically using density function theory (TD-DFT)[17].
Semi-empirical methods like (PM6 and PM7) and density function theory using basis set (B3LYP) were applied in the studying of the complexation between the tyrosine with β-cyclodextrin compound. The eigenvalues (HOMO and LUMO) and the thermodynamics parameters were evaluated and compare these data with experimental[18].
Complexation of some amino acid (Try, His and Phe) with isonitro-soacetophenone compound have been synthesized and characterized using different techniques. The spectroscopic (IR, UV-vis and ESR), electrochemical (cyclic voltammetry) and theoretical

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calculations (DFT methods) were used to study the complexation of the amino acids[19].

Another complexation were found at interaction between the phenyl-alanine and different kinds of transition metals Cd(II), Zn(II), Co(II) and Cu(II). The physico-chemical properties of the complex have been evaluated using theoretical calculation, UV-Vis, thermo-gravimetric and IR were applied in the characterization of the interactions[20].
Also, the biological activity of the complexation of the adenine compound with numbers of transition metals have been carried out, theses metals were characterized and identification using conductivity, TGA and spectroscopic methods[21,22].

2. Experimental:

Polarographic equipment (Metohm 797VA) was used phosphate buffer solution as supporting electrolyte at pH=7. Square wave voltammetry (SWV) was applied for recording the peak current of the complexation using three electrode system consists of platinum (2mm) as a working electrode and (1.5 mm) Pt wire as an auxiliary electrode and Ag/AgCl immersed in saturated KCl as a reference electrode. The inert nitrogen gas was used for bubbling the solution to remove the dissolve oxygen and mixed the solutions in the cell.

The quantum calculations were performed by GAUSSIAN 03 software package. The optimization of the geometry was done suing Hartree-Fock (HF) method at (STO-3G) as basis set.
The tyrosine compound and the cadmium chloride were used in this study which are used in pure compounds.

3. Results and Discussion:

The interaction voltammetric data of the complexation were collected. A constant amount of the cadmium metal (II) was added into voltammetric cell a sequence concentrations of tyrosine were added. The peak current of the cadmium metal (II) was decrease immediately with an increasing of the tyrosine concentration , the result are summarized in table (1). To calculate the binding constant depend on the following equation[23]:

$$\ln\left(\frac{Ip}{Ip^{o}-Ip}\right) = \ln\left(\frac{1}{[tyrosine]}\right) - lnK \quad \text{---------(1)}$$

Where :
K = binding constant
Ip^{o} = peak current of metal
Ip = peak current of amino acid

The plot of the ln((Ip/Ip°-Ip)) against the ln(1/[tyrosine]), gives the intercept which represent the (-lnK) in the equation(1).
Later, the measurements were repeated at temperatures range from 283K to 313K

Table 1. Effect of adding tyrosine to the cadmium (II) at (313K)

Conc. of Cd (M)	Ep (V)	Correct (Ip^{o})(A)
1.48E-04		1.74E-05
Conc of Tyr (M) $x10^{-5}$	Ep (V)	Correct (Ip)(A) x 10^{-5}
1.17	-0.768	1.600
1.36	-0.768	1.490
1.55	-0.774	1.290
1.74	-0.774	0.713
1.93	-0.786	0.537
2.12	-0.803	0.315
2.31	-0.797	0.229
2.50	-0.732	0.197

The effect of the temperatures on the complexation was studied and the biding constant was calculated for each temperature in the in the range of the temperatures (293-313 K). From the figure (1) we can notice clearly a sequence decrease in the current peak (Ip) with increasing temperatures.

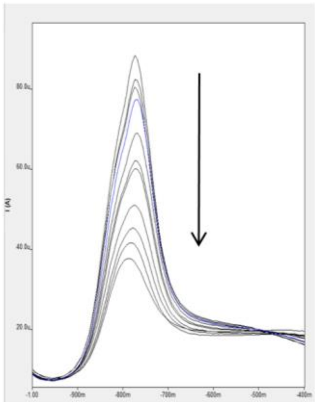

Fig 1. Square wave voltammograms of a sequence addition of tyrosine to the cadmium solution

Table (2) change to the values the lnK values for all temperatures range. We can notice that there are increase in the lnK value which increasing temperatures.

Table 2. Values of the temperatures, lnK and correlation coefficient for complexation

Temp. (K)	**Ln K**	**R**
293	14.372	0.9964
298	35.333	0.9652
303	40.312	0.9959
308	67.165	0.9495
313	71.283	0.9798

Figure (2) shows the linear relation between the (lnK) against the (1/T). the plot of (lnK) versus (1/T) gives a straight line with correlation coefficient (R2= 0.9521). From the values of the thermodynamics parameters we can notice that (ΔG) become more negative with temperature increasing. This mean that at an increasing of the temperature lead to increase the spontaneity of complexation. Which is lead to increase of complexation and increasing of binding constant. The positive value of the enthalpy change indicates that the complexation interaction was endothermic which mean that the complexation process increase with increasing temperatures. Finally, the positive value of the entropy (ΔS) was mention to the more random process of the complex.

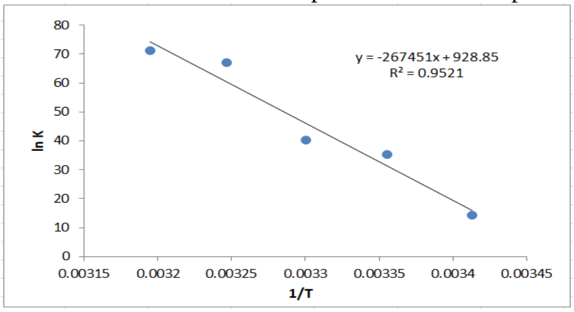

Fig. 2. Van't Hoff equation for complex between cadmium and tyrosine

The thermodynamic functions for the complexation interaction were determined. The entropy (ΔS), the enthalpy (ΔH) and the Gibbs free energy (ΔG) have been evaluated using Van't Hoff equations (2) which summarized in table (3):

$$lnK = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \text{ ------- } (2)$$

Where :

K = Binding constant (M^{-1})

R = universal gas constant (8.314 x 10^{-3} kJ/mol^{-1}/K^{-1})

T = Absolute temperature (K)

Table 3. Thermodynamic parameters for interaction of cadmium with tyrosine at temperatures range (293-313 K)

Temp (K°)	Binding constant (K_b) (M^{-1})	ΔH (KJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})	ΔG° (KJ.mol^{-1})
293	1.745E+06			-35.010
298	2.213E+15			-87.541
303	3.216E+17	2223.588	7722.459	-101.552
308	1.477E+29			-171.990
318	9.074E+30			-185.498

The computational calculation of the complex between the tyrosine with cadmium metal has been studied using the Hartree-Fock method (HF) at basis set STO-3G. Also, the physic-chemical properties were evaluated beside the thermodynamic parameters. Tables (4, 5 and 6) were showed the bond length, bond angle and torsion for the complex of tyrosine with cadmium which appear clearly at figure (3).

Table 4. Bond length for the complexation of tyrosine-cadmium

Bond	Value	Bond	Value	Bond	Value
(1,12)	1.23	(7,33)	1.08	(16,38)	1.09
(1,13)	1.33	(8,9)	1.39	(17,18)	1.53
(2,3)	1.50	(8,10)	1.39	(17,39)	1.09
(2,27)	2.29	(9,34)	0.99	(17,40)	1.09
(2,28)	1.03	(10,11)	1.39	(18,19)	1.39
(2,47)	1.03	(10,35)	1.08	(18,24)	1.39
(3,4)	1.55	(11,36)	1.08	(19,20)	1.38
(3,29)	1.09	(13,27)	1.95	(19,41)	1.08
(4,5)	1.53	(14,16)	1.59	(20,21)	1.39
(4,30)	1.09	(14,25)	1.23	(20,42)	1.08
(4,31)	1.09	(14,26)	1.33	(21,22)	1.39
(5,6)	1.40	(15,16)	1.50	(21,23)	1.39
(5,11)	1.39	(15,27)	2.29	(22,43)	0.99
(6,7)	1.38	(15,37)	1.03	(23,24)	1.38
(6,32)	1.08	(15,46)	1.03	(23,44)	1.08
(7,8)	1.40	(16,17)	1.55	(24,45)	1.08
				(26,27)	1.95

Table 5. Bond angle for the complexation of tyrosine-cadmium

Angle	**Value**	**Angle**	**Value**	**Angle**	**Value**	**Angle**	**Value**
(12,1,13)	125.5	(5,6,32)	119.4	(16,15,46)	109.2	20,19,41)	119.1
(3,2,27)	103.0	(7,6,32)	119.3	(27,15,37)	112.7	19,20,21)	119.9
(3,2,28)	109.3	(6,7,8)	119.9	(27,15,46)	118.9	19,20,42)	120.9
(3,2,47)	108.4	(6,7,33)	121.1	(37,15,46)	105.2	21,20,42)	119.2
(27,2,28)	122.2	(8,7,33)	119.0	(14,16,15)	108.4	20,21,22)	117.5
(27,2,47)	108.7	(7,8,9)	117.4	(14,16,17)	110.0	20,21,23)	119.4
(28,2,47)	104.7	(7,8,10)	119.3	(14,16,38)	109.2	22,21,23)	123.1
(2,3,4)	113.1	(9,8,10)	123.3	(15,16,17)	109.9	21,22,43)	105.4
(2,3,29)	105.9	(8,9,34)	105.4	(15,16,38)	110.1	21,23,24)	120.0
(4,3,29)	109.2	(8,10,11)	120.0	(17,16,38)	109.2	21,23,44)	119.7
(3,4,5)	113.1	(8,10,35)	119.9	(16,17,18)	113.4	24,23,44)	120.3
(3,4,30)	108.9	(11,10,35)	120.2	(16,17,39)	108.9	18,24,23)	121.2
(3,4,31)	107.2	(5,11,10)	121.3	(16,17,40)	107.3	18,24,45)	119.6
(5,4,30)	109.9	(5,11,36)	119.8	(18,17,39)	109.7	23,24,45)	119.2
(5,4,31)	110.4	(10,11,36)	118.9	(18,17,40)	109.9	14,26,27)	116.9
(30,4,31)	107.2	(1,13,27)	117.5	(39,17,40)	107.5	2,27,13)	82.7
(4,5,6)	120.6	(16,14,25)	118.6	(17,18,19)	121.2	2,27,15)	102.4
(4,5,11)	121.3	(16,14,26)	115.8	(17,18,24)	120.6	2,27,26)	113.7
(6,5,11)	118.1	(25,14,26)	125.6	(19,18,24)	118.2	3,27,15)	114.0
(5,6,7)	121.3	(16,15,27)	102.1	(18,19,20)	121.3	3,27,26)	154.3
		(16,15,37)	108.3	(18,19,41)	119.6	5,27,26)	82.9

Table 6. Torsion for the complexation of tyrosine-cadmium

Torsion	Value	Torsion	Value	Torsion	Value	Torsion	Value
(12,1,13,27)	160.2	(4,5,11,10)	-179.1	(25,14,26,27)	-158.9	(40,17,18,19)	-136.8
(27,2,3,4)	-157.9	(4,5,11,36)	1.4	(27,15,16,14)	34.7	(40,17,18,24)	43.8
(27,2,3,29)	82.6	(6,5,11,10)	0.1	(27,15,16,17)	-85.6	(17,18,19,20)	-179.2
(28,2,3,4)	70.8	(6,5,11,36)	-179.4	(27,15,16,38)	154.1	(17,18,19,41)	1.3
(28,2,3,29)	-48.7	(5,6,7,8)	0.0	(37,15,16,14)	-84.4	(24,18,19,20)	0.1
(47,2,3,4)	-42.8	(5,6,7,33)	179.8	(37,15,16,17)	155.3	(24,18,19,41)	-179.3
(47,2,3,29)	-162.3	(32,6,7,8)	-179.6	(37,15,16,38)	34.9	(17,18,24,23)	179.3
(3,2,27,13)	19.1	(32,6,7,33)	0.2	(46,15,16,14)	161.5	(17,18,24,45)	-1.0
(3,2,27,15)	-94.0	(6,7,8,9)	-179.9	(46,15,16,17)	41.2	(19,18,24,23)	-0.1
(3,2,27,26)	178.4	(6,7,8,10)	0.1	(46,15,16,38)	-79.2	(19,18,24,45)	179.6
(28,2,27,13)	142.2	(33,7,8,9)	-0.4	(16,15,27,2)	-133.4	(18,19,20,21)	-0.1
(28,2,27,15)	29.2	(33,7,8,10)	-179.7	(16,15,27,13)	139.2	(18,19,20,42)	-179.8
(28,2,27,26)	-58.4	(7,8,9,34)	-178.7	(16,15,27,26)	-20.6	(41,19,20,21)	179.4
(47,2,27,13)	-95.7	(10,8,9,34)	1.4	(37,15,27,2)	-17.4	(41,19,20,42)	-0.4
(47,2,27,15)	151.2	(7,8,10,11)	-0.1	(37,15,27,13)	-104.8	(19,20,21,22)	179.9
(47,2,27,26)	63.6	(7,8,10,35)	179.7	(37,15,27,26)	95.4	(19,20,21,23)	-0.1
(2,3,4,5)	-62.5	(9,8,10,11)	179.8	(46,15,27,2)	106.4	(42,20,21,22)	-0.3
(2,3,4,30)	60.0	(9,8,10,35)	-0.4	(46,15,27,13)	19.0	(42,20,21,23)	179.7
(2,3,4,31)	175.6	(8,10,11,5)	0.0	(46,15,27,26)	-140.8	(20,21,22,43)	178.8
(29,3,4,5)	55.1	(8,10,11,36)	179.5	(14,16,17,18)	179.4	(23,21,22,43)	-1.3
(29,3,4,30)	177.6	(35,10,11,5)	-179.7	(14,16,17,39)	-58.1	(20,21,23,24)	0.1
(29,3,4,31)	-66.8	(35,10,11,36)	-0.3	(14,16,17,40)	57.9	(20,21,23,44)	-179.7
(3,4,5,6)	-76.0	(1,13,27,2)	1.8	(15,16,17,18)	-61.3	(22,21,23,24)	-179.8
(3,4,5,11)	103.2	(1,13,27,15)	102.1	(15,16,17,39)	61.2	(22,21,23,44)	0.4
(30,4,5,6)	162.1	(1,13,27,26)	-130.1	(15,16,17,40)	177.3	(21,23,24,18)	0.0
(30,4,5,11)	-18.7	(25,14,16,15)	140.3	(38,16,17,18)	59.6	(21,23,24,45)	-179.7
(31,4,5,6)	44.1	(25,14,16,17)	-99.5	(38,16,17,39)	-177.9	(44,23,24,18)	179.8
(31,4,5,11)	-136.7	(25,14,16,38)	20.4	(38,16,17,40)	-61.9	(44,23,24,45)	0.1
(4,5,6,7)	179.1	(26,14,16,15)	-41.6	(16,17,18,19)	103.1	(14,26,27,2)	99.3
(4,5,6,32)	-1.2	(26,14,16,17)	78.6	(16,17,18,24)	-76.3	(14,26,27,13)	-134.5
(11,5,6,7)	-0.1	(26,14,16,38)	-161.6	(39,17,18,19)	-18.9	(14,26,27,15)	-1.1
(11,5,6,32)	179.5	(16,14,26,27)	23.2	(39,17,18,24)	161.8		

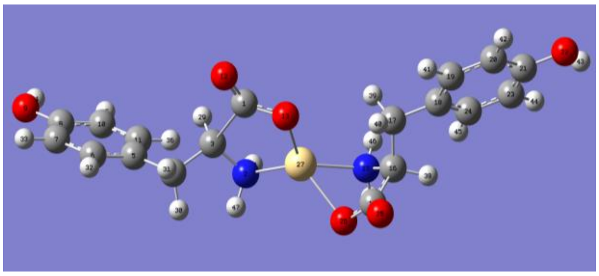

Fig. 3. The optimization form of the complex $[(Tyr)_2Cd]$

The calculated of the complexation energy between the products and the reactants (2-Tyrosine + metal $\rightarrow$ Complex) was appear at equation (3).

$E_{complexation} = E_{complex} - [(E_{tyrosine})_2 + E_{Cd}]$ ------- (3)

Table 7. Thermodynamic values for the cadmium, tyrosine and complexation

	E (a.u.)	ΔE (a.u.)	ΔH (a.u.)	ΔG (a.u.)	E (Thermal) KCal/Mol
Cd	0.01	0.01609	0.01703	0.00698	10.09
Tyr	0.22	0.23565	0.23660	0.18457	147.87
Cd+2Tyr	0.40	0.42102	0.42196	0.33719	264.19
H2O	0.02	0.02721	0.02816	0.00664	0.02
$E_{Complexation}$	-0.0402	-0.0391	-0.0401	-0.0323	-24.5750

At comparison between the theoretical calculation with the experimental values, we can a proof that there are somewhat compact or match in the data. At table (7), the ΔG value at (298 K) it about (-84.80 KJ/mol) which is somewhat near to the free energy data at table (3) for the $E_{complexation}$ (-98.19 Kj/mol). Where, the theoretical calculations were determined at the room temperature (298 K).

4. Conclusion:

The voltammetric results were show there are increase in the peck current of the tyrosine with adding more concentration of cadmium. Thais phenomena indicate that the complexation was produce at increasing of the metal. This complexation was studied at a range of the temperature (293-313 K) and calculate the thermodynamic parameters.

The results of the thermodynamics values show that spontaneous and the endothermic of the complexation between the metal with the amino acid at increasing of the temperatures. The theoretical calculations describe the conformation and configuration of the complex between the tyrosine with cadmium which having the formula $[(Tyr)_2Cd]$.

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