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# Electrochemical and Thermodinamic Study of Tyrosine and its Complexes in Aqueous solution by conductivity measurement

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Abstract: The electrical conductivities of aqueous solutions of tyrosine was measured, in the beginning Kohlrausch equations was used to discover types of electrolyte through plot the relation between equivalent conductivity against the square root of molar concentration for tyrosine at 310.16K. The plot indicate that amino acid was weakly associated in water the molar conductivity of tyrosine measured by processing the obtained data using the conductivity equation of lee-Wheaton to calculation of the ionic molar conductivity  $(\Lambda)(64.9)$ , the association constant (KA)(218610), distance parameter (R)(1.00E-06), stander and deviation  $(\sigma \Lambda)(0.91)$  the analysis shows that cation is association with anion to form contact ion -pair (CIP). The prepared complexes of tyrosine with Co(II), Mn(II), Ni(II), Fe(II), to form [Ni(tyr)3]Cl2, [Co(tyr)3]Cl2, [Fe(tyr)3]Cl2, [Mn(tyr)3]Cl2 complexes are measured using in the temperature range from (288.16–313.16K) in steps of 5 K. To give information about ionic molar conductivity ( $\Lambda$ ), the association constant (KA), distance parameter (R), and standard deviation ( $\sigma\Lambda$ ). Standard thermodynamic information from association and examining the nature of the interaction was obtained and calculation of the thermodynamic quantities ( $\Delta H^{\circ}$ ,  $\Delta G^{\circ}, \Delta S^{\circ}$ ) have been done. A multi parameter curve fitting procedure is used to give the lowest value of curve fitting parameter,  $\sigma(\Lambda)$ , between the experimental and calculated values The values differ from one complex in to another depending on the interactions in solution, the values of stander deviation proved that lee-wheaton equation suitable for this study.

Keywords:Tyrosine, Tyrosine complexes, Electrical conductivities, Lee-Wheaton equation, Thermodynamic parameter

# Introduction

Amino acids are very important for human body for their regular biological activities. Amino acids are the building blocks of the body. Besides building cells and repairing tissue, they forms antibody to combat bacteria and virus; they are part of enzyme and hormonal system. Amino acids are very important for building nucleoproteins (RNA & DNA) (Hames et al., 2005)<sup>[1]</sup>. Eight amino acids areregards essential for human body: phenylalanine, valine, Threonine, Tryptophan, Isoleucine, Methionine, Lucien, and lysine (Ferrmand et al., 2001)<sup>[2]</sup> Additionally, Histidine and Arginine are required by infants and growing children (Adugana et al., 2004)<sup>[3]</sup> .Tyrosine intake in their food because the person living with Phenylketonuria PKU can't convert the Phenylalanine into Tyrosine .Many amino acids and their derived complexes were prepared and identified by using different methods (ex: spectral (U.V,IR), magnetic susptibility, elemental analysis and X-ray diffraction], since amino acids as ligands contain two donor atoms (N and O), therefore the complexes of amino acids with metals are interesting to study, here are some applications in this area The complexes of Ca(II), Ni(II), Fe(II) with mixed ligands of amino acids (Glycine, Histidine, Cysteine and Arginine) were prepared and identified by elemental analysis, electrochemical conductivity measurements at different temperatures at PH=7,the thermodynamic data were calculated then the conductivity data were compared with other electrical method(Abdel –Rahman, et al., 2007)<sup>[4]</sup>. Molar conductivities of dilute solutions for the complexes: Co(II)(alanine + valine),Ni(II)(valine + serine), Ca(II)(alanine + serine), Mg(II)(valine + serine) in water were measured in the temperature range from (293.16–313.16K) The ionic molar conductivity( $\Lambda$ ), the association

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constant (KA), distance parameter (R), were determined by treating experimental data with Lee-Wheaton conductivity equation. Thermodynamic quantities for the ion association reaction were derived from the Temperature(Al-Allaf, *et al.*, 2013)<sup>[5]</sup>. Using the expanded Lee-Wheaton equation of electric conductivity, constants of ionic association are defined. It is determined that LiClO4 in propylene carbonate is a nonassociated electrolyte. In order to account on the dynamics of jonic solvation, separation into jonic components is made, Results of conductometric investigations of solutions of several 1-1 electrolytes in propylene carbonate in the range of temperatures from 298 to 398 K are presented (Chernozhuk, et al., 2016) [6]. The electrical conductivities of aqueous solutions of quinic acid and its sodium salt were measured from 293.15 to 328.15 K in steps of 5 K. The molar conductivities of the sodium salt were treated by the Lee-Wheaton equation in the form of Pethybridge and Taba, and the Kohlrausch equations. The limiting molar conductivities of the quinate anion were estimated, as well as the corresponding ionic association constants and standard thermodynamic functions of the ionic association reaction. The hydrodynamic radius of the quinate anion was calculated from the Walden rule and compared with the van der Waals radius(Kloutar, et al., 2007)<sup>[7]</sup>. The molar conductivities of dilute solutions of potassium chloride in binary mixtures of ethanol and water were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The experimental data were treated by the Lee-Wheaton conductivity equation and parameters  $\Lambda_0$  and  $K_A$  derived. The ionic limiting molar conductivities ( $\lambda_0$ ) were obtained using the literature values of the cation limiting transference number  $to(K^{+})$  from the same temperature range. The ionic Walden product  $(\lambda_0 \eta)$ , thermodynamic quantities for the ion-association reaction  $(\Delta G^{\circ}, \Delta H^{\circ} \text{ and } \Delta S^{\circ})$  and the activation enthalpy of the ionic movement were calculated and discussed in terms of the ionic size, as well as solvent viscosity, permittivity, structure and basicity (Boskovic, et al., 2013)<sup>[8]</sup>.

#### **Experimental**

Conductivity water was prepared by redistilling water three times with the addition of little amount of potassium permanganate and a small pellets of (KOH) (Palmer,1954)<sup>[9]</sup>. The complexes of Fe(II),Co(II), Mn(II) and Ni(II) with tyrosine was prepared by mixing (0.001mole,0.1988g) of (FeCl<sub>2</sub>.4H<sub>2</sub>O) , (0.001mole,0.2378g) from (CoCl<sub>2</sub>.4H<sub>2</sub>O), (0.001mole,0.238g) from (NiCl<sub>2</sub>.4H<sub>2</sub>O) and (0.001mole,0.197g) from (MnCl<sub>2</sub>.4H<sub>2</sub>O) in 25 ml of conductivity water with (0.003 mole,0.5435g) of the amino acid Tyrosine in 25 ml of conductivity water and refluxed for about two hours on cooling, each complex was precipitated. Magnetic electronic spectra, IR measurement was used to make sure of the resulting complexes . A general method has been used for measuring the conductance of the electrolytes, the conductivity cell was washed , dried and then weighed empty and kept at a constant temperature ( $\pm$  0.1°C) using a water circulating ultra thermostat . A certain amount of solution was injected into the conductivity meter. Another known amount of solution was injected by a syringe of 1ml and the measurement was repeated. Generally about (15) addition have been made by weighing the amount for each one.

#### **Results and Discussion**

It was found that Lee-Wheaton equation is applicable to the interpretation of conductance data for simple (2:1 + 1:1) in water at 298.16K [9]. This equation is used for complete analysis of mixed symmetrical and asymmetrical electrolyte at different temperatures. The electrical conductivity of the amino acid solution of tyrosine was studied in conductivity water, which was subtracted from acid continuation values, at 310.16 K .the tyrosine solution promised symmetrical electrolytes of type (1:1) if the positive ion is denoted by(M<sup>+</sup>) and negative ion (X<sup>-</sup>)when using the equation for these solution can be explain as follows.

$$\begin{array}{ccc} M^{+}_{aq.} + X^{-}_{aq.} & Ka \\ Ka: association constant \end{array} \xrightarrow{(M_{aq}^{+n} X)}$$

Kohlrausch has established the stability that the solution are weak electrolytes after electrical conductivity was measured at the above –mentioned temperature of the mother acid solution .the intent used is then to calculated the equivalent concentration for tyrosine solution using a special calculation program to extract the equivalent continuity after entering the conductivity information, physical parameter, temperature and weights of the additives, as it was shown that amino acid under study the behavior of the weak electrolytes was demonstrated by the relationship between the square root of the different concentration of the tyrosine solution versus the equivalent continuation calculated through the calculation program. Values indicating that solution behave like weak electrolytes(Dabbagh and Akrawi, 1992)<sup>{10}</sup>, figure (1) demonstrates this behavior . The lee-Wheaton equation was applied to the amino acid solution described above , where the equivalent conductivity was

calculation program after it announced the electrical conductivity of all studied fixed cell concentration (0.5cm), density (0.99707gm/cm3), the data including concentration and equivalent conductivity values, were analyzed using aspecial analysis software after giving information on both absolute temperature (T), viscosity of solution (0.0089pois) and dielectric constant (78.3D). after completing the analysis of the data it was confirmed that these solution were weak electrolytes .as a result of the the analysis The ionic molar conductivity (A) ( 64.9), the association constant (Ka)( 218610), distance parameter (R)( 1.00E-06) and stander deviation ( $\sigma$ A)( 0.091). The analysis shows that cation is associated with anion to form contact ion –pair (CIP) ((Lee and Wheaton 1978))<sup>[11]</sup>. The values of stander deviation proved that lee-wheaton equation suitable for this study.

Conc. Mole/L*10 <sup>7</sup>	$\sqrt{ ext{Conc.}}$ Mole/L*10 <sup>3</sup>	$\frac{\Lambda}{(Ohm^{-1}.equive^{-1}.cm^2)}$
5.076851	0.712520245	98.48611
10.22603	1.01123835	78.89477
14.80581	1.216791272	60.65571
19.71295	1.404028134	52.046
24.55657	1.567053605	45.72224
29.27562	1.711011981	40.39238
33.99138	1.843675134	39.15806
38.60946	1.964929006	37.41918
43.29933	2.080849106	37.7599
47.86036	2.187701076	36.37544

Table 1. Molar concentration (M) and Equivalent conductance of Tyrosine in water at 310.16K



Figure 1. Molar concentration (M) and Equivalent conductance of Tyrosine in water at 310.16K

The following mixtures are chosen for this study. The equivalent conductivity ( $\Lambda_{equiv.}$ ) at each concentration of each electrolyte solution was calculated by the following equation: ( $\Lambda_{equiv.}$ ) = 1000 $\sigma$  / C<sub>1</sub>C<sub>2</sub> ......(1)

Where  $\sigma$  is the specific conductance obtained experimentally,  $C_1$  and  $C_2$  are the equivalent concentration of 2:1 and 1:1 electrolytes used respectively. The values of the equivalent conductivity and concentrations of the two electrolytes salts (2:1 and 1:1) determined experimentally.

$$\begin{array}{c} M^{2^+} + X^- \\ MX^+ + X^- \end{array} \xrightarrow{KA1} MX^+ \\ \overbrace{KA2} MX_2 \end{array}$$

For each mixture there are four ionic species ( $M^{+2}$ ,  $X^{-1}$ ,  $MX^+$  and  $MX_2$ ) ions. The theoretical equivalent conductance is given by the following equation.

Where  $Z_i$  is the charge, mi molar concentration,  $\lambda_i$  equivalent conductivity for each ionic species present in the solution and  $C_n$  is the stoichiometric equivalent concentration of electrolyte species n. It was found earlier that Ka and  $\Lambda$  value for single ion and for ion - pair are constant from one system to another for symmetrical, asymmetrical and mixed electrolytes by using lee-Wheaton equation (Lee and Wheaton (1978)<sup>[12]</sup>. Therefor the values of concentration and( $\Lambda$ ) in Tables and figures (2) (a-d) . The input data of computer program are solvent parameters (T, D,  $\eta$ ), charges Zi and limiting conductivities  $\lambda^{\circ}i$  for each ionic species.

	Λ	Λ	Λ	Λ	Λ	Λ
Conc.	(Ohm <sup>-1</sup> . equive <sup>-</sup>					
Mole/L*10 <sup>7</sup>	<sup>1</sup> .cm <sup>2</sup> ) 288.16 °K	<sup>1</sup> .cm <sup>2</sup> ) 293.16 °K	<sup>1</sup> .cm <sup>2</sup> ) 298.16 °K	<sup>1</sup> .cm <sup>2</sup> ) 303.16 °K	<sup>1</sup> .cm <sup>2</sup> ) 308.16 °K	<sup>1</sup> .cm <sup>2</sup> ) 313.16 °K
2.383897	209.740	136.878	208.055	199.19	191.741	221.59
5.007807	133.125	99.0153	133.776	135.87	132.808	134.626
7.418538	112.331	90.2398	114.315	99.921	99.3843	102.543
9.521729	105.022	85.0816	114.454	84.774	85.4115	87.4339
11.88098	98.1961	80.4602	110.892	70.063	69.2089	84.0921
14.21494	93.7980	77.7961	108.193	58.007	67.8131	70.7315
16.45612	91.1515	75.6954	108.938	49.586	60.0880	70.8832
18.75926	88.8450	73.3356	107.429	44.019	58.7973	67.2633
20.90903	87.6814	73.6221	103.099	45.014	54.7795	66.7278
23.19345	86.2312	72.675	99.2228	42.747	49.6143	66.2269
	250			-	T=288.16C	
	<b>~</b> 200 -	<b>t</b>			T=293.16C	
	<b>T</b> .	M)		$\sim$	T-208 16C	

Table 2a. Molar concentration (M) and Equivalent conductance of  $[Co(C_9H_{11}NO_3)_3]Cl_2$  in water at different temperatures



Figure 2a. The relation between the square root of concentration and the equivalent conductance of  $[Co (C_9H_{11}NO_3)_3]Cl_2$  at different temperatures

Table 2b. Molar concentration (M) and Equivalent conductance of  $[Fe(C_9H_{11}NO_3)_3]Cl_2$  in water at different temperatures

Conc. Mole/L*10 <sup>7</sup>	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 288.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 293.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 298.16 °K	Λ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 303.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 308.16 °K	Λ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 313.16 °K
2.760822	181.1058	202.7705	185.529	238.5023	129.3583	133.6344
5.345241	144.7216	128.8271	127.284	159.0835	114.7457	99.238
7.828444	126.4495	108.4458	106.9917	129.653	86.67001	88.69511
10.22255	114.1267	99.24797	99.3177	99.54557	76.7261	80.94354
12.40562	107.4781	94.9043	92.5799	93.2404	66.28027	75.5241
14.95515	100.2999	90.84052	88.34605	89.97767	60.57096	70.57441
17.39708	101.3817	87.1188	86.21001	88.00488	58.50777	70.23684
19.52292	102.9806	85.79326	84.29774	85.76924	57.16596	65.07155
21.87674	101.2766	85.52024	85.75169	85.75169	56.12665	64.30665
24.15812	102.3839	86.74034	85.94481	76.55907	56.72736	64.81703



Figure 2b. The relation between the square root of concentration and the equivalent conductance of  $[Fe (C_9H_{11}NO_3)_3]Cl_2$  at different temperatures

Conc. Mole/L*10 7	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 288.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 293.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 298.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 303.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 308.16 °K	Λ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 313.16 °K
2.511813	129.0591	136.2342	130.475	127.288	134.4554	125.075
4.914812	120.6442	126.8353	120.872	114.005	124.9509	95.4786
7.384514	112.8486	116.3184	111.441	107.831	109.3058	89.1087
9.615788	103.9956	106.1697	102.569	100.205	100.9905	84.8022
12.01134	97.13045	100.0837	96.6024	99.459	94.97099	81.5334
14.39375	92.63277	95.80995	92.0740	98.4071	89.70667	75.3756
16.53605	90.71085	92.44804	90.3886	97.0306	88.50784	71.2534
18.78537	88.72146	89.94707	89.2522	96.4747	86.47475	69.2593
21.03257	87.16635	89.4364	87.0967	95.7865	85.18074	67.9267
23.18772	86.25257	88.00122	86.1609	95.0657	83.99399	66.1585

Table 2c. Molar concentration (M) and Equivalent conductance of [Mn(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> in water at different temperatures

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Figure 2c. The relation between the square root of concentration and the equivalent conductance of  $[Mn (C_9H_{11}NO_3)_3]Cl_2$  at different temperatures

Table 2d. Molar concentration (M) and Equivalent conductance of [Ni(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> in water at different temperatures

Conc. Mole/L*10 <sup>7</sup>	Λ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 288.16 °K	Λ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 293.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 298.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 303.16 °K	A (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> ) 308.16 °K	Λ (Ohm <sup>-1</sup> . equive <sup>-</sup> <sup>1</sup> .cm <sup>2</sup> ) 313.16 °K
2.472517	134.815	152.337	219.969	208.65	209.369	202.769
4.565327	111.262	111.262	141.322	109.20	108.038	104.586
7.05793	90.8423	72.9625	119.120	73.190	71.8239	71.2649
9.301885	77.9064	64.9064	89.7624	65.354	58.2693	63.6543
11.58103	64.5653	59.3859	82.4796	58.616	56.0497	56.0497
13.71313	60.7689	56.6456	73.0953	49.620	56.7080	54.0393
15.94772	58.7048	52.9220	73.6707	42.517	55.462	52.1944
18.21375	54.9035	51.5446	74.1549	37.465	55.6294	45.9321
20.38609	53.0530	50.1801	66.4267	33.077	51.9870	48.7971
22.63517	51.5422	50.0065	63.0171	33.349	51.8041	44.4636



Figure 2d. The relation between the square root of concentration and the equivalent conductance of [Ni (C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> at different temperatures

In Generally it can be observed the equivalent conductance ( $\Lambda$ ) of Fe>Co>Ni>Mn compelexes gave higher value in the rang of temperatures between (293.16-303.16). Probably because of the effect of the temperature on the properties of solution and with increase the degree of temperature decrease the density and the viscosity and may be increase association and decrease equivalent conductance ( $\Lambda$ ) because effect of the asymmetric effect(or relaxation effect (Dabbagh and Akrawi, 1992)<sup>{10}</sup>.

Tables 3(a-d) show the results of the analysis compelexes at different temperatures. where each table show the association constant (KA) and the equivalent conductance ( $\Lambda$ ), the(R) values (distance parameter) and the best fit data standard deviation  $\sigma$ s( $\Lambda$ ).

Table 3a. the values at constant Ka,  $\Lambda$ , the distance between R(A°) and  $\sigma\Lambda$  of the[Co(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> at different temperatures in water solvent

T(K)	Ka	$\Lambda$ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> )	R(A°)	σΛ
288.16	1781	42	4	0.032
293.16	3201	45	8	0.015
298.16	9602	52	5	0.046
303.16	10440	35	4	0.112
308.16	11380	26	4	0.068
313.16	12001	18	8	0.063

Table 3b. the values at constant Ka, A,the distance between  $R(A^\circ)$  and  $\sigma \Lambda$  of the  $[Fe(C_9H_{11}NO_3)_3]Cl_2$  at different temperatures in water solvent

T(K)	Ka	$\Lambda$ (Ohm <sup>-1</sup> . equive <sup>-1</sup> .cm <sup>2</sup> )	R(A°)	σΛ					
288.16	5610	52	8	0.059					
293.16	11010	36	7.9	0.063					
298.16	14110	36	4	0.053					
303.16	14502	34	4	0.116					
308.16	15802	39	4	0.074					
313.16	17702	18	8	0.047					

Table 3c. the values at constant Ka,  $\Lambda$ , the distance between R(A°) and  $\sigma\Lambda$  of the[Mn(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> at different temperatures in water solvent

	uniterent te	mperatures in we	ater sorreite	
T(K)	Ka	$\Lambda (Ohm^{-1}. equive^{-1}.cm^2)$	R(A°)	σΛ
288.16	16601	42	5	0.114
293.16	9810	46	8	0.073
298.16	8410	38	8	0.064
303.16	6610	42	8	0.026
308.16	6300	36	8	0.057
313.16	5910	20	4	0.069

T(K)	Ka	$\Lambda (\text{Ohm}^{-1}, \text{equive}^{-1}, \text{cm}^2)$	R(A°)	σΛ
288.16				
202.16	42100	10	4	0.063
293.16	43701	5	8	0.138
298.16	10701	U	0	01100
	45100	6	5	0.143
303.16	50100	2	0	0.070
308 16	50100	3	8	0.069
508.10	58001	5	4	0.046
313.16				
	64810	3	4	0.045

Table 3d. the values at constant Ka,  $\Lambda$ , the distance between R(A°) and  $\sigma\Lambda$  of the[Ni(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub> at different temperatures in water solvent

In tables 3(a-d) the values of  $\lambda M^{2+}$  deferent rom complex to another depend on the values of equivalent conductance ( $\Lambda$ ) and Ka value of Ni>Mn>Co>Fe complexes because the electronic density of the element increase associations with decrease the radii of metal this mean that the solvent molecules will be attracted and thus ion association increase, The results of distance parameter R show that complexes electrolytes form solvent separated ion pairs (R is between4-8) these high values of R indicated that cations and anions are separated by many solvent molecules since the association was high with increase temperatures(Hemes, P.J., 1974)<sup>[12]</sup>. The values of  $\sigma\Lambda$  give an indication of good best-fit values (Akrawi, B.A. *,et al*, 2008)<sup>[13]</sup>.

#### Calculation of the thermodynamic parameters ( $\Delta$ H, $\Delta$ G, $\Delta$ S)

The relation of lnKA against 1/T was shown in figure 3 (a-d) and the relation between them was illustrated by Vant-Hoff equation(Eggers *et al.*, 1964)<sup>[14]</sup>.

 $\ln Ka = -\frac{\Delta H}{RT} + C$ 

The relation gives a straight line for complex solutions, This behavior will be illustrated by the fact that the results of association depends on two opposite effects. The first one was the formation of ion pairs separated by solvent molecules (SSIP) and the other was the formation of contact ion pairs (CIP) (Dawod, 1995)<sup>{15}</sup>. The values of  $\Delta$ H were calculated from Vant –Hoff equation and  $\Delta$ G from the equation :

 $\Delta G = -R T \ln KA$ 

While  $\Delta S$  values were calculated from the equation :

 $\Delta G = \Delta H - T \Delta S$ 

From the tables below, the values of  $\Delta H$  (enthalpy of association) were negative which show that the operation was hydration ,while  $\Delta G$  (Gibbs free energy) has a negative values which depends upon the kind of ions and in agreement with the relation

### $\Delta G = -RTLnKA$

which means that the reaction was spontaneous towards association , and the values of  $\Delta S$  were also negative due to the negative values of  $\Delta H$  which leads to the ordering of the system as a result of association under the influence of solvation and columbic effect in spontaneous continuum media (Nancollas, 1960)<sup>{16}</sup>.

Table 4a. Thermodynamic parameters of [Co(C <sub>9</sub> H <sub>11</sub> NO <sub>3</sub>						
Т		$-\Delta S$	-ΔG	$-\Delta H$	Ln ka	
(K)	(J.m	$ol^{-1}.K^{-1}$ )	(KJ.mol <sup>-1</sup> )	(KJ.mol <sup>-1</sup> )		
288.	16	140	17.92	58.13	7.485	
293.	16	131	19.66		8.071	
298.	16	119	22.72		9.17	
303.	16	115	23.31		9.253	
308.	16	111	23.92		9.34	
313.	16	108	24.44		9.393	



Figure 3a. The relation between the Ln ka &1/T of  $[Co(C_9H_{11}NO_3)_3]Cl_2$ 

Т	$-\Delta S$	-ΔG	-ΔH	Ln ka
(K)	$(J.mol^{-1}.K^{-1})$	$(KJ.mol^{-1})$	$(KJ.mol^{-1})$	
288.16			29.69	
	20.67	20.67		8.632
293.16				
	22.67	22.67		9.307
298.16				
	23.67	23.67		9.555
303.16				
200.16	24.14	24.14		9.582
308.16	2476	24.76		0.669
212 16	24.76	24.76		9.008
515.10	25 16	25 46		0 791
	25.40	23.40		9.701

Table 4b. Thermodynamic parameters of [Fe(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub>



Figure 3b. The relation between the Ln ka &1/T of  $[Fe(C_9H_{11}NO_3)_3]Cl_2$ 

Table 4	Table 4c. Thermodynamic parameters of $[Mn(C_9H_{11}NO_3)_3]Cl_2$							
Т	$-\Delta S$	-ΔG	$\Delta H$	Ln ka				
(K)	$(J.mol^{-1}.K^{-1})$	$(KJ.mol^{-1})$	(KJ.mol <sup>-1</sup> )					
	``````````````````````````````````````	. ,						
288.16			29.09					
	-20.2	23.27		9.717				
293.16								
	-22.9	22.39		9.191				
298.16								
	-22.5	22.39		9.037				
303.16								
	-22.9	22.16		8.796				
308.16								
	-21.7	22.4		8.748				
313.16								
	-20.7	22.6		8.684				



Figure 3c. The relation between the Ln ka &1/T of [Mn(C<sub>9</sub>H<sub>11</sub>NO<sub>3</sub>)<sub>3</sub>]Cl<sub>2</sub>

Table 40. Thermodynamic parameters of $[141(C_911_{11}14O_3)_3]C_{12}$				
Т	$-\Delta S$	-ΔG	-ΔH	Ln ka
(K)	$(J.mol^{-1}.K^{-1})$	$(KJ.mol^{-1})$	$(KJ.mol^{-1})$	
× ,		· · · ·	· /	
288.16			13.24	
	42 55	25.5		10.65
203 16	12.35	20.0		10.05
295.10	10.51			10.00
	43.64	26.03		10.69
298.16				
	44.66	26.55		10.72
303 16				
505.10	16.07	27.26		10.00
	46.27	27.26		10.82
308.16				
	48.2	28.09		10.97
313.16				
010110	40.91	20.02		11.00
	49.81	28.83		11.08
40				

Table 4d. Thermodynamic parameters of  $[Ni(C_9H_{11}NO_3)_3]Cl$ 



Figure 3c. The relation between the Ln ka &1/T of  $[Ni(C_9H_{11}NO_3)_3]Cl_2$ 

# Conclusion

The present work reports conductivity data for the low concentration tyrosine solutions in water at 310.16 K. The electrical conductivities of Co, Fe, Mn, Ni complex with tyrosine in water at different temperatures were measured by using of lee-Wheaton equation at the best fit values of standard deviled ( $\Box \Box \Box \Box$  for analyzing the data of unsymmetrical electrolytes including: The equivalent conductivity  $\Lambda$ , the association constant KA and the distance parameter R. The values differ from one complex to another depending on the interactions in solution and effect the electrophoretic, asymmetric effect and the type of metal.

### Recommendations

The lee-wheaton equation is very important, it be used to determination of any ionic compound at very low concentration, with any solvent at different temperatures and give information about association constant

KA, equivalent conductivity at infinity dillution  $\Lambda_{\circ}$  and the distance parameter R, Which is very important constant in Thermodynamic. Thermodynamic parameters can be calculated by using Vant-Hoff equation from association constant.

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