

Electrical Conductance Study of Glutamic Acid Complex with [Mn(II)] in Different Solvents and Temperatures

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Abstract: The electrical conductivities of glutamic acid complex with [Mn(II)] was study in different solvents (water, methanol, ethanol) 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 at different temperature from (288.16 -313.16) kilven. The plot indicate that complex of amino acid was weakly associated in different solvents and temperatures. The molar conductivity of glutamic acid complex measured by processing the obtained data using the conductivity equation of Lee-Wheaton equation to calculation the Equivalent conductance at infinite dilution (Λ_0), The association constant (KA), distance parameter (R), and standard deviation ($\sigma\Lambda$). Thermodynamic information from association and examining the nature of the interaction was obtained and calculation of the standard thermodynamic quantities have be measure. 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. An iterative numerical method which was found to be very successful has been used to find the minimum ($\sigma\Lambda$), show the results of analysis that complex ions were separated by solvent molecules (SSIP). The values of (KA), (Λ_0) and (R) differ from solvent to another depending on the interactions in solution. The Walden product (Λ_1) for this complex have been studied in water, methanol and ethanol.

Keywords: Glutamic acid, Glutamic acid complex with [Mn(II)], Electrical conductivities, Lee-Wheaton equation, Thermodynamic parameter

Introduction

Thermodynamic properties are very useful study of the intermolecular interactions and geometrical effects in the systems and thermo-physical and bulk properties of solutions, Studying the information of the transport properties (conductance, viscosity, ionic mobility) of electrolytes in aqueous and partially aqueous media tell us all about ion-ion and ion-solvent interactions in these solutions (Wagner, 2012). The Lee-Wheaton equation which is one of the mathematic equations of conductivity theories has been successfully used to investigate many electrolytes in solutions (Lee & Wheaton, 1978). The physical properties of the binary mixed solvents like the viscosity and the relative permittivity can be varied making them more favor to solvent system for the study of ion association and ion mobility (Al-Healy, 2020). Many amino acids and their derived complexes were prepared and identified by using different methods since amino acids as ligands contain two donor atoms (N and O) (William, 2012), therefore the complexes of amino acids with metals are interesting to study. The conductivity of Tyrosine has been studied in aqueous solutions at 310.16K, 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 (Λ), the association constant (KA), distance parameter (R), and standard deviation ($\sigma\Lambda$) and the thermodynamic quantities (ΔH° , ΔG° , ΔS°) have been calculation (Al-Healy & Hamed, 2019). 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, 2007). The complexes of Co(II), Zn(II) with mixed ligands of amino acids (systine, histidine, systine methyl ester and histidine methyl ester) were prepared

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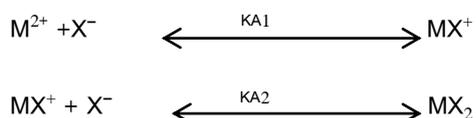
and identified by elemental analysis, electrochemical conductivity, magnetic measurements and IR spectra (Rabindra, et al., 2005¹). Molar conductivities of dilute solutions for the complexes: Co(II)(alanine + valine), Ni(II)(valine + serine), Ca(II)(alanine + serine), Mg(II)(valine + serine) in water were measured in the temperature range from (293.16–313.16K). The ionic molar conductivity (Λ), the association constant (KA), distance parameter (R), and ($\sigma\Lambda$) at best fit values were determined by treating experimental data with Lee-Wheaton conductivity equation. Thermodynamic quantities for the ion association reaction were derived from the temperature dependence of KA. The obtained results provide information on ion – ion and ion-solvent interactions (Al-Allaf, et al., 2013). 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 non-associated electrolyte. In order to account on the dynamics of ionic solvation, separation into ionic 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 & Kalugin, 2016). *Glutamic acid* is an amino acid occurring in substantial amounts as a product of the hydrolysis of proteins. Certain plant proteins (e.g., gliadin) yield as much as 45 percent of their weight as glutamic acid; other proteins yield 10 to 20 percent. Much of this content may result from the presence of a related substance, glutamine, in proteins; glutamine is converted to glutamic acid when a protein is hydrolyzed. First isolated in 1865 (Okubo, *et al.*, 2010), glutamic acid is an important metabolic intermediate. It is one of several so-called nonessential amino acids; i.e., animals can synthesize it from oxoglutaric acid (formed in the metabolism of carbohydrates) and do not require dietary sources. Monosodium glutamate (MSG), a salt of glutamic acid, is sometimes used as a condiment for flavouring foods (Flickinger, 2010).

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). The complex of Mn(II) with glutamic acid was prepared by mixing (0.001 mole, 0.125g) from (MnCl₂.4H₂O) in 25 ml of conductivity water with (0.003 mole, 0.4414g) of glutamic acid in 25 ml of conductivity water and refluxed for about two hours. On cooling, each complex was precipitated (Hummodat & Mustafa, 2013). 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 ($\pm 0.1^\circ\text{C}$) using a water circulating ultra thermostat. A certain amount of solution was injected into the conductivity cell and the conductivity of solution was measured by WTW Inolab 740 computerized conductivity meter. Another known amount of solution was injected by a syringe of 1ml and the measurement was repeated. Generally about (14) addition have been made by weighing the amount for each one.

Results and Discussion

Conductometric data were treated using Lee-Wheaton equation in which a wide dielectric range for electrolytes solution can give detailed information concerning ion-ion and ion-solvent interaction.



Ka: association constant

For unsymmetrical electrolyte 2:1 a program (RM1) is used to analyze the concentration- conductivity measurements in which the input data are (T, D, η) where T is temperature in Kelvin, D and η are the dielectric constant and viscosity (poise) of the solvent at (37oC). Lee and Wheaton obtained an equation of unsymmetrical electrolytes of the form (Lee & Wheaton, 1979).

$$\Lambda = \Lambda_o [1 + C_1(KR)(\epsilon K) + C_2(KR)(\epsilon K)^2 + C_3(KR)(\epsilon K)^3 - (PK / (1 + KR)) \{1 + C_4(KR)(\epsilon K) + C_5(KR)(\epsilon K)^2 + KR / 12\}]$$

All the terms are defined in the original paper (Lee & Wheaton, 1978). The program (RM1) is used to determine values of KA, Λ^o and R where KA is the association constant; R is the average center to center distance for the

ion pairs; Λ° , is the equivalent conductance of each ion in solution. A multi parameter "Least square" curve fitting procedure is used to give the lowest value of curve fitting parameter, ($\sigma\Lambda$), between the experimental and calculated values. An iterative numerical method which was found to be very successful has been used to find the minimum ($\sigma\Lambda$).

Therefore the Tables (1) (a-c) and figures (A)(1-3) show the relations between (Λ) and concentration (\sqrt{c}) for the studied complexes at different temperatures. A general look at the tables of the solution complexes of amino acids with Mn(II) at different temperatures and at different solvent shows that the equivalent conductance(Λ) increases with increasing temperatures, 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 (Dabbagh & Akrawi,1992).

Table 1a. Molar concentration (M) and equivalent conductance of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in water at different temperatures

Conc. Mole/L*10 ⁻⁷	Λ	Λ	Λ	Λ	Λ	Λ
	(Ohm- 1 . equive-1.cm2) 288.16 °K	(Ohm- 1 . equive-1.cm2) 293.16 °K	(Ohm- 1 . equive-1.cm2) 298.16 °K	(Ohm- 1 . equive-1.cm2) 303.16 °K	(Ohm- 1 . equive-1.cm2) 308.16 °K	(Ohm- 1 . equive-1.cm2) 313.16 °K
3.0419	190.8092	186.5064	187.2148	190.5933	192.4664	190.2133
5.5837	162.4498	158.8135	127.5207	162.2564	131.0804	129.553
8.2203	151.2950	147.9345	106.0480	151.1059	108.9931	107.7291
10.4578	149.3133	146.0206	97.6883	149.1180	100.3888	99.22949
12.8893	146.0287	142.8327	91.2036	145.8294	93.7122	92.63486
15.4092	144.5078	141.3914	86.9463	144.2940	89.3260	88.3037
17.8822	143.9474	141.0144	85.1083	143.7427	87.4271	86.43068
20.1587	137.2175	141.0390	83.2094	143.8778	85.4656	84.49575
22.2411	136.2117	140.8209	81.7194	143.8409	83.9246	82.97646
24.6559	136.9926	140.7240	80.8314	143.5502	83.0026	82.06878
27.3819	135.6228	140.2216	80.4530	142.9758	81.6064	80.69244
29.8709	134.7634	140.5403	79.4821	138.5195	81.5974	80.68699
32.3825	134.4476	140.2063	79.2155	134.2039	81.3141	80.41058
34.2517	130.1749	140.2204	78.6700	129.9319	80.7443	79.85097

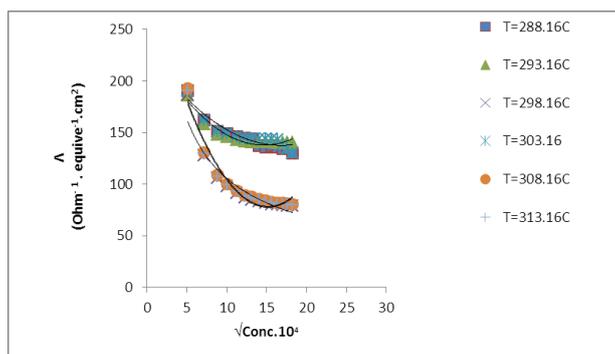


Figure 1a. Equivalent conductance of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in water at different temperatures

Table 1b. Molar concentration (M) and Equivalent conductance of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in methanol at different temperatures

Conc. Mole/L*10 ⁻⁷	Λ	Λ	Λ	Λ	Λ	Λ
	(Ohm- 1 . equive-1.cm2) 288.16 °K	(Ohm- 1 . equive-1.cm2) 293.16 °K	(Ohm- 1 . equive-1.cm2) 298.16 °K	(Ohm- 1 . equive-1.cm2) 303.16 °K	(Ohm- 1 . equive-1.cm2) 308.16 °K	(Ohm- 1 . equive-1.cm2) 313.16 °K
2.6837	124.2027	126.5987	128.4337	126.0031	127.5169	123.8668
5.2189	95.8047	97.5994	99.0139	97.1759	98.3379	95.5342
7.71234	64.8308	50.2506	66.9655	65.7465	66.5290	64.6396
10.0287	49.8562	39.3153	51.4703	50.5513	51.1503	49.7030
12.6141	43.8527	34.0451	40.8987	44.4473	40.6569	39.5113
15.2023	41.8051	31.2963	38.8931	40.1831	33.7268	32.7804
17.6669	39.6379	26.0004	34.6279	38.2398	29.0149	28.2040
19.9337	37.7351	22.3996	34.4525	34.0819	25.7097	24.9937
22.4324	37.1486	21.3782	33.9170	30.9444	22.8406	22.2071
24.7648	36.6691	19.8737	32.1771	33.8855	20.6847	20.1132
27.2709	33.8573	19.4369	31.4292	30.1057	18.7795	18.2628
29.5357	33.6498	17.9657	30.5986	28.5667	17.3357	16.8604
31.9319	31.3166	17.6812	30.0905	26.4185	16.0312	15.5935
34.1291	29.3004	16.6366	29.0045	24.7136	14.9958	14.5879

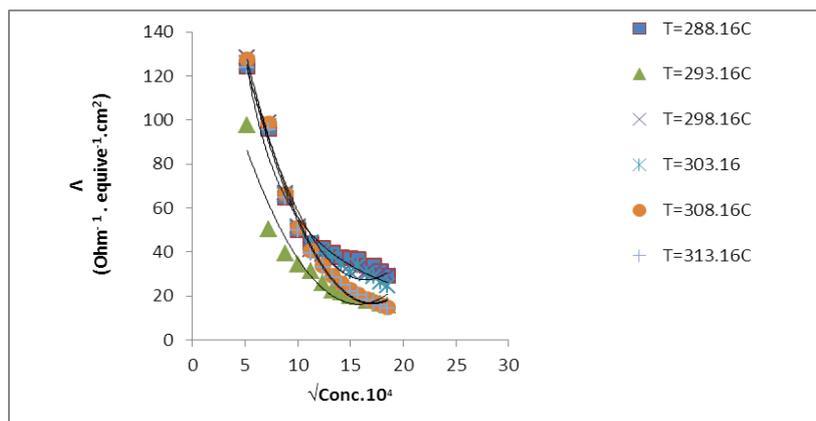


Figure 1b. Equivalent conductance of $[Mn(C_5H_7NO_4)_3]Cl_2$ in methanol at different temperatures

Table 1c. Molar concentration (M) and Equivalent conductance of $[Mn(C_5H_7NO_4)_3]Cl_2$ in ethanol at different temperatures

Conc. Mole/L*10 ⁻⁷	Λ	Λ	Λ	Λ	Λ	Λ
	(Ohm- 1 . equive- 1.cm2) 288.16 °K	(Ohm- 1 . equive- 1.cm2) 293.16 °K	(Ohm- 1 . equive- 1.cm2) 298.16 °K	(Ohm- 1 . equive- 1.cm2) 303.16 °K	(Ohm- 1 . equive- 1.cm2) 308.16 °K	(Ohm- 1 . equive- 1.cm2) 313.16 °K
4.9886	65.8186	66.1697	59.3676	67.0649	67.3797	67.5368
10.4565	30.8780	31.6332	29.7871	33.1230	33.2812	32.2180
15.1464	22.0073	21.8826	28.5462	31.9908	32.1422	32.1422
20.0693	16.6090	16.5479	22.6503	24.9944	25.1148	25.1755
24.9671	13.3508	19.9922	18.3425	20.0884	20.1860	20.2353
30.0471	12.6012	16.6447	15.3532	16.6898	16.7715	16.8129
34.9044	11.2307	14.3562	13.3119	14.3652	14.4361	14.4722
39.6784	11.0936	12.6532	11.7932	13.5278	13.5961	12.7300
44.5205	10.1215	11.2984	10.5840	12.6350	12.6350	11.3446
49.3997	9.5498	10.2016	9.6042	12.2880	12.2880	10.2234
54.3762	9.1951	9.2851	8.7844	11.2593	12.3506	9.2870
59.1615	8.4514	8.5498	8.1276	11.2926	11.3158	8.5352
63.6382	7.8569	7.9628	7.6054	10.4968	10.5510	7.9348
68.2427	7.3267	7.4389	7.1380	9.78730	9.78730	7.398449

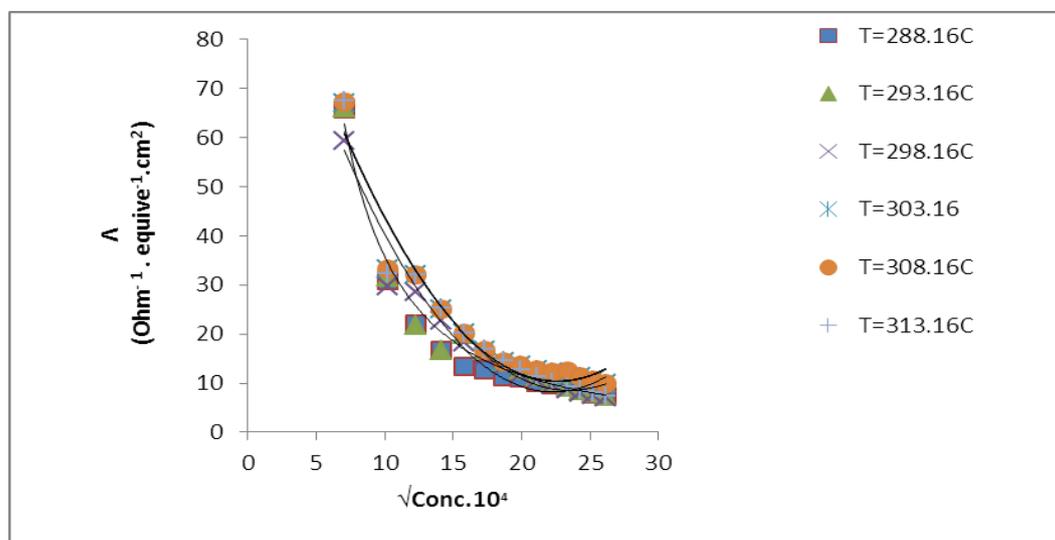


Figure 1c. Equivalent conductance of $[Mn(C_5H_7NO_4)_3]Cl_2$ in ethanol at different temperatures

It was found that equivalent conductivity at different temperatures decrease with in crease concentration. This may be understand as discussed by (Lee & Wheaton, 1978). That in water (D~79) and in presence of hydrogen

bonding and we show the equivalent conductivity of water > methanol > ethano, the solvation will be higher in water more than methanol and ethanol because of the effects of viscosity and dielectric constant at different temperatures. The Lee-Wheaton equation was applied to the complex solution described above, where the equivalent continuity was a 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 a special 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 solutions were weak electrolytes. Tables 2(a-c) show the results of the analysis complexes at different temperatures, where each table shows the association constant (K_a) and the equivalent conductance (Λ), the (R) values (distance parameter) and the best fit data standard deviation σ(Λ).

Table 2a. the values at constant K_a, Λ, the distance between R(A°) and σΛ of [Mn(C₅H₇NO₄)₃]Cl₂ at different temperatures in water

T (K)	K _a	Λ° (Ohm ⁻¹ . equi ⁻¹ .cm ²)	R (A°)	σΛ
288.16	210	92	50	0.048
293.16	260	80	4.0	0.019
298.16	310	64	7.9	0.069
303.16	360	42	4.5	0.036
308.16	420	36	5.0	0.072
313.16	470	30	4.0	0.070

Table 2b. the values at constant K_a, Λ, the distance between R(A°) and σΛ of [Mn(C₅H₇NO₄)₃]Cl₂ at different temperatures in methanol

T (K)	K _a	Λ° (Ohm ⁻¹ . equi ⁻¹ .cm ²)	R (A°)	σΛ
288.16	100	18	6.0	0.009
293.16	130	15	5.0	0.010
298.16	150	12	8.0	0.027
303.16	170	11	5.0	0.026
308.16	210	10	5.0	0.033
313.16	260	6	7.9	0.035

Table 2c. the values at constant K_a, Λ, the distance between R(A°) and σΛ of [Mn(C₅H₇NO₄)₃]Cl₂ at different temperatures in ethanol

T (K)	K _a	Λ° (Ohm- 1 . equi ⁻¹ .cm ²)	R (A°)	σΛ
288.16	31	16	9.5	0.045
293.16	61	14	8.4	0.042
298.16	80	12	5.4	0.041
303.16	110	10	5.5	0.037
308.16	130	8	5.0	0.036
313.16	160	6	9.4	0.034

We also note the K_a value of complexes because the electronic density of the solvent decreases associations with decrease that the solvent molecules will be attracted and thus ion association increases. The results of distance parameter R show that complexes electrolytes form solvent separated ion pairs (R is between 4-8) these high values of R indicated that cations and anions are separated by many solvent molecules since the association was high with increase temperatures. The values of σΛ give an indication of good best-fit values (Akrawi, et al, 2008).

Calculation of the Thermodynamic Parameters (ΔH, ΔG, ΔS)

The values of ΔH were calculated by the relation between lnK_a against 1/T illustrated by Vant-Hoff equation (Eggers et al., 1964).

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

The relation gives a straight line for complex solutions, and ΔG from the equation : $\Delta G = - R T \ln K_A$

While ΔS values were calculated from the equation : $\Delta G = \Delta H - T \Delta S$

From the tables below, the values of ΔH (enthalpy of association) were negative which show that the operation was hydration ,while ΔG (Gibbs free energy) has a negative values which depends upon the kind of ions and in agreement with the relation: $\Delta G = - RT \ln K_A$ which means that the reaction was spontaneous towards association , and the values of ΔS were small positiv due to the negative values of ΔH 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.

Table 3a. Thermodynamic parameters of $[Mn(C_5H_7NO_4)_3]Cl_2$ at different temperatures in water

T (K)	ΔS (J.mol ⁻¹ .K ⁻¹)	$-\Delta G$ (KJ.mol ⁻¹)	$-\Delta H$ (KJ.mol ⁻¹)	Ln ka
288.16	39.2	12.80	24.1	5.34
293.16	360	13.55		5.56
298.16	33.2	14.21		5.73
303.16	30.6	14.83		5.88
308.16	28.0	15.47		6.04
313.16	25.9	16.01		6.15

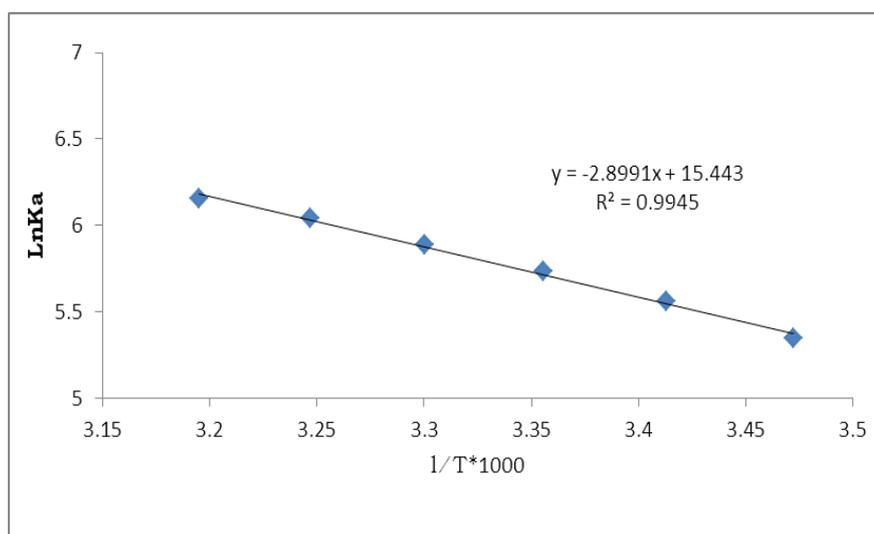


Figure 2a. The relation between the Ln ka & 1/T of $[Mn(C_5H_7NO_4)_3]Cl_2$ in water

Table 3b. Thermodynamic parameters of $[Mn(C_5H_7NO_4)_3]Cl_2$ at different temperatures in methanol

T (K)	ΔS (J.mol ⁻¹ .K ⁻¹)	$-\Delta G$ (KJ.mol ⁻¹)	$-\Delta H$ (KJ.mol ⁻¹)	Ln ka
288.16	132.56	11.03	27.15	4.60
293.16	133.13	11.86		4.88
298.16	132.77	12.41		5.11
303.16	132.70	12.94		5.13
308.16	132.60	13.69		5.37
313.16	132.97	14.47		5.56

In water, the values of ΔH° are negative and ΔS° are positive, this will ascribed to specific short-range interaction such as hydrogen bonding. the values of ΔS° and in methanol are positive and ΔH° are negative may mean that the temperature dependence of D,

$$\Delta H_{eq}^\circ = -bRT^2(T-1 + \partial \ln D / \partial T) (d \ln K_A / db)$$

$\partial \ln D / \partial T$ represent how much the ion solvation is weakened by ion association. The positive value of ΔS° in Table 3 has been considered as due to the decreased orientation of solvent molecules when the ion pair performed.

In ethanol the value of ΔH° is negative and ΔS° positive because of the low value of the dielectric constant of ethanol which leads to ion solvent interaction, and the high value of association constants leads to very low value of Λ° of $[\text{Mn}(\text{glu})_3]^{2-}$ ion and more orientation due to ion solvent interaction.

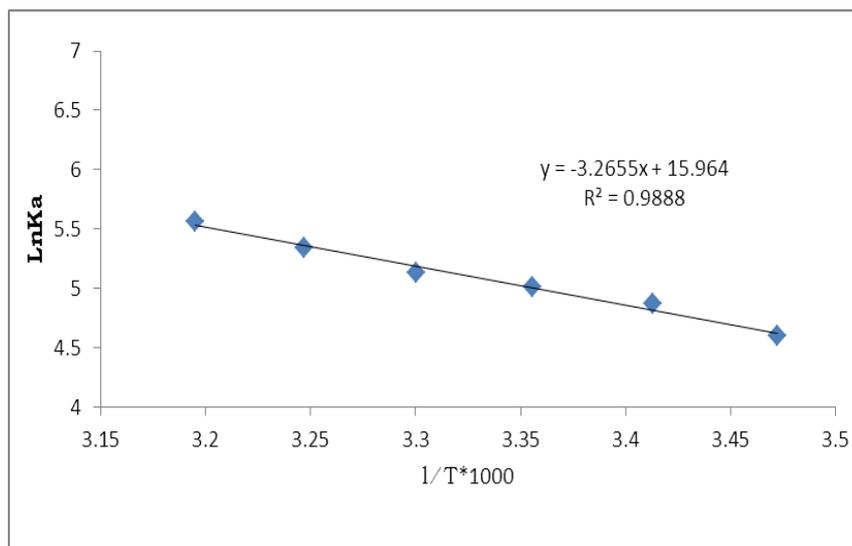


Figure 2b. The relation between the Ln ka & 1/T of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in methanol

Table 3c. Thermodynamic parameters of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ at different temperatures in ethanol

T (K)	ΔS (J.mol ⁻¹ .K ⁻¹)	$-\Delta G$ (KJ.mol ⁻¹)	$-\Delta H$ (KJ.mol ⁻¹)	Ln ka
288.16	198.95	8.22	46.48	3.43
293.16	192.82	10.01		4.11
298.16	192.41	10.86		4.38
303.16	192.49	11.84		4.70
308.16	191.39	12.47		4.86
313.16	190.70	13.21		5.07

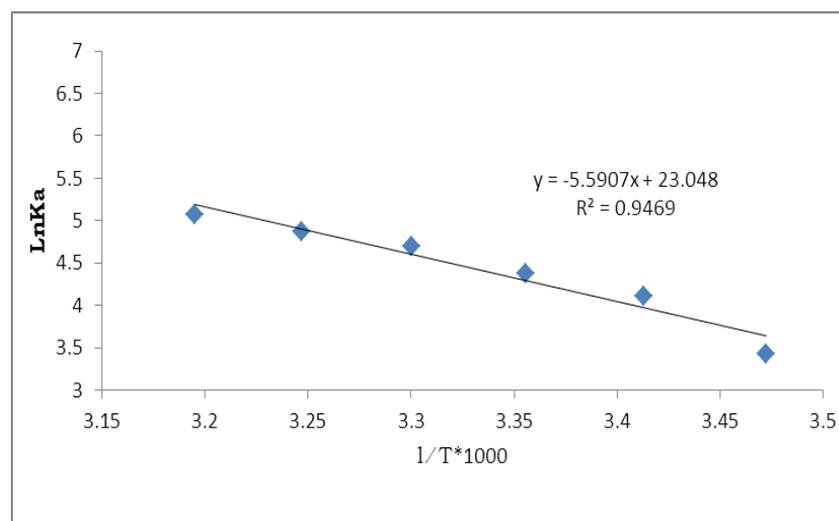


Figure 2c. The relation between the Ln ka & 1/T of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in ethanol

Walden product

The Walden product ($\Lambda_0\eta$) for studied complexes have been calculated in water, methanol and ethanol were obtained by multiplying each values of Λ from Table 2 by the appropriate viscosity in the temperature range 283.15 - 313.15 K (Al-Healy & Hameed, 2020). We can show the effect of viscosity and density from solvent to other at different temperature. All results are listed in Table 4.

Table 4. The Walden product ($\Lambda_0\eta$) parameters of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in water, methanol and ethanol at different temperatures

T(K)	$(\Lambda_0\eta)$		
	$[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in water	$[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in methanol	$[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in ethanol
288.16	0.6108	0.1110	0.2160
293.16	0.5104	0.0862	0.1680
298.16	0.3916	0.0645	0.1320
303.16	0.2461	0.0554	0.1003
308.16	0.2016	0.0474	0.0720
313.16	0.1620	0.0268	0.0498

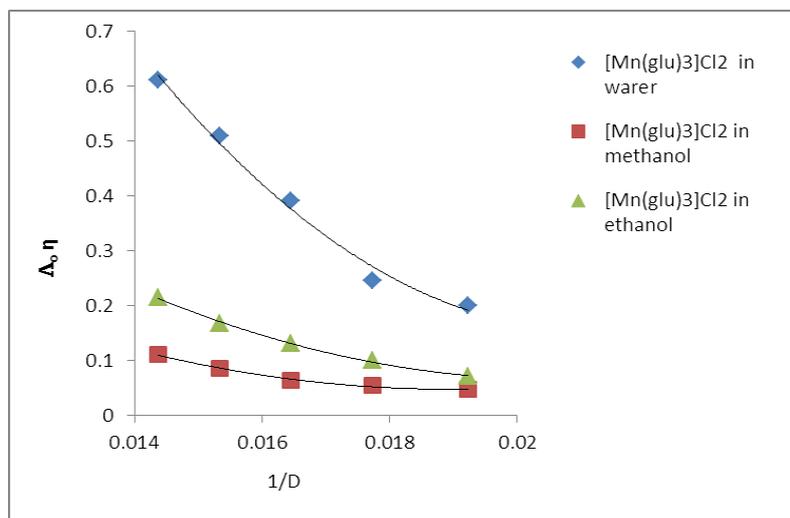


Figure 3. The Walden product ($\Lambda_0\eta$) parameters of $[\text{Mn}(\text{C}_5\text{H}_7\text{NO}_4)_3]\text{Cl}_2$ in water, methanol and ethanol at different temperatures

Walden product ($\Lambda_0\eta$) of the complex at different temperature against $1/D$ is shown in Figure(3). It is clear that ($\Lambda_0\eta$) decrease with decreasing D . The increase of D of the solvent will increase the solvating power of that solvent. This causes that the ion will move with only the primary solvation shell in the solvent and the effect of the secondary solvation appears to be very small (Doe and Kitagaw, 1985)^[19]. Thus the size of the primary solvated ion is expected to be smaller in the order: $\text{MeOH} < \text{EtOH} < \text{H}_2\text{O}$. The ion association constant K_A (1) increase with decreasing D of the solvent due to the multiplestep association process with solvation and desolvation of $[\text{Mn}(\text{glu})]$ (Vesna, S. et al., 2008)^[20].

Conclusion

The present work reports conductivity data for the low concentration glutamic acid with Mn solutions in water, methanol and ethanol at different temperature. Lee-Wheaton equation at the best fit values of standard deviation (σ) for analyzing the data of unsymmetrical electrolytes including: The conductivity parameters, the association constant K_A and the distance parameter R . The values differ from solvent to another depending on dielectric constant and viscosity and interactions in solution the effect of electrophoretic effect or asymmetric effect.

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 K_A , equivalent conductivity at infinity dilution Λ° 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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