Conductometric Study of Proline-Mn (II) Complex in Some Solvents at Various Temperatures, with Computational Factors Calculation

Fanar M Al-Healy¹, Shayma H Abdulrahman¹* and Anfal R Mahmoud¹

Department of Chemistry, College of Science, University of Mosul.

*E-mail: shaymaa.hashim@uomosul.edu.iq

Abstract: The equivalent conductivities of proline in water, methanol were studied in the temperature range of 288.15 to 313.15 K at 5 K intervals, in mixtures of methanol and water at percentages of 10%, 20%, 30%, 40% and, 50% of methanol at 37°C. The experimental data were treated by the Lee-Wheaton conductivity equation of unsymmetrical electrolytes (1:2) (1 molecule of metal with 2 molecules of ligand) derived to calculate the conductivity parameters, equivalent conductance at infinite dilution Λₒ, ionic conductivity, association constant Ka and the main distance between ions in solution (R) at best fit values of (ϬΛ). Thermodynamic quantities for the ion-association reaction (∆Gₒ, ∆Hₒ and ∆Sₒ) have been also measured. The results of the analysis showed that the ions of the complex can be separated by solvent molecules (SSIP). The values of Ka, Λₒ and R were found to be different from one solvent to another depending on the interactions in the solution. Furthermore, the chemical structure of the Proline-Mn complex was optimized by using of Gaussian interface version 16.0 program of chem3D to optimiz the features of complex molecule. The suggested statistical model possesses only two parameters with excellent values of the square regression coefficient (r²) and cross-validation (q²) are equal to 0.999 and 0.994, respectively, which refers to the perfect relationship between Ka value and the physical properties of the solvent.

Keywords: Proline Complex, Electrical Conductivities, Lee-Wheaton equation, Thermodynamic parameter, Gaussian program, Semi-empirical.

1. Introduction:
Proline (Pro), composed of an amino group and a carboxylic acid, is an amino acid. It is the only amino acid with a secondary alpha-amino group that naturally exists, which explains its more basic character with respect to many other alpha-amino acids. Pro and its derivative in organic reaction are also used as asymmetric catalysts. It is an osmoprotectant and is also used in many biotechnological and medicinal applications [1]. The biological function of several transition metals with mixed amino acid complexes have been revealed, putting them in many biochemical processes [2–5]. Pro has been estimated in different ways such as HPLC [6–8], flow-injection analysis [9], kinetic study [10], capillary electrophoresis [11] in addition to theoretical study [12,13]. The complexes of amino acids
with metals are interesting to be studied by electrical methods especially by conductivity methods. For example, the Tyrosine conductivity has been studied in aqueous solutions at 310.16 K, also Co(II)-, Mn(II)-, Ni(II)-, Fe(II)-prepared tyrosine complexes to form [Ni(tyr)3]Cl2, [Co(tyr)3]Cl2, [Fe(tyr)3]Cl2, and [Mn(tyr)3]Cl2 complexes at various temperatures. Numerous complexes of Co(II), Ni(II) and Fe(II) with different ligands of amino acids (e.g. Glycine, Histidine, Cysteine and Arginine) were prepared and diagnosed using various techniques and then studying their electrochemical conductivity in several solvents [14-15].

The electrical conductivity of solutions depends on the nature of the solute and solvent. For a solvent, the main parameter is the dielectric constant [16]. It is interest to study the effect of temperature and solvent on the electrical conductivity of complexes [17]. In this study, Molar conductivities of dilute solutions for the complex: Mn(II)(Proline) in water, methanol and mixture of them were measured in the temperature range (288.15 - 313.15 K ). The ionic molar conductivity (Λ), association constant (Ka) and distance parameter (R), were determined by treating experimental data with Lee-Wheaton conductivity equation.

Hence, the ion-association thermodynamic quantities (∆G °, ∆H ° and ∆S °) are a very useful study of intermolecular interactions, geometric influences of solutions structural, thermo-physical and bulk properties. The study of the transport properties (conductance, viscosity,density and ionic mobility) of electrolytes in aqueous and partly aqueous media. It provides us more detail about ion-ion and ion-solvent interactions in these solutions especially from thermodynamic point of view [18,19].

All Computational Details using semi-empirical methods with the Gaussian’09 software package were carried out. Semi-empirical approaches adopt what are sometimes referred to as empirical techniques where there is no clear using of the two-electron component of the Hamiltonian. Roald Hoffmann suggested the expanded Huckel approach for all valence electron systems. Chem 3D ultra-program were used for a graphic presentation, and to optimized using semi empirical quantum chemical computation [20].

2. Experimental
The Mn(II) complex with proline was prepared by mixing 0.001mole (0.1258g) of MnCl2.4H2O in 25ml of conductivity water, its conductivity was equal (2μS), with 0.003 mole (0.3439g) of the proline in 25 ml of conductivity water and refluxed for two hours. On cooling, the complex was precipitated. Magnetic electronic spectra, IR measurement were used to investigate composition of complex [21]. Conductivity water was prepared by redistilling water three times with the addition of 1.5g/L KmnO4 and 0.05g/L KOH [22]. A general method eas used for measuring the conductivity of the electrolytes. The conductivity cell was washed , dried and then weighted empty and kept at a constant temperature (± 0.1ºC) 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 (1ml) and the measurement was repeated. Generally about (15) addition have been made by weighting the amount for each one.

2.1 Computational details
Theoretical calculations were carried out using GAUSSIAN 09 package software implemented on a Lenovo-PC computer with a 2.6 GHz processor. Initial estimation of the structural geometry of the prolin complex was obtained by a molecular mechanic methods (MM2, MD), and for further optimization of geometry, we used the AM1 then PM3 method. Finally, Statistical analysis of the experimental results was performed, using Minitab software release 14.1 to find a mathematical equation that describe the relationship between the Ka and the important solvent properties (dielectric constant and viscosity) of the mix methanol and water at different percentages.

3. RESULTS AND DISCUSSION
3.1. Molecular Geometry Optimization
Geometry optimization was carried out to determine the best atomic arrangement that makes the molecule more stable. Optimized geometrical parameters such as bond lengths and bond angles and dihedral angles of proline-Mn(II) complex were calculated by semi empirical methods using
parameter PM3[23]. The optimized structures with atom labeling and number labeling of complex are shown in Figure 1.

![Figure 1. Semi-empirical-calculated optimized structure (at PM3 level of theory) of Proline-Mn complex](image)

After minimizing the energy, the molecule will be in minimum energy level (more stable), then was determine the internal coordinates of atoms of the complex molecule as shown in the Table 1. After that measured the Huckel charge, from the Huckel charge measurement on each atom of complex molecule, we can deduce that the manganese atom have the largest amount of charge, followed by the three nitrogen atoms.

**Table 1.** PM3-calculated bond lengths and angles between all atoms of the complex molecule.

| Atom   | Bond atom | bond length (Å) | Angle Atom (°) | 2nd Angle Atom (Å) | 2nd Angle (°) | 2nd Angle Type |
|--------|-----------|-----------------|----------------|--------------------|---------------|----------------|
| C(3)   | N(4)      | 1.438           |                |                    |               |                |
| Mn(25) | N(4)      | 1.846           | C(3)           | 104                |               |                |
| N(12)  | Mn(25)    | 1.846           | N(4)           | 90                 | C(3)          | -127.488       | Dihedral       |
| N(20)  | Mn(25)    | 1.846           | N(4)           | 90                 | N(12)         | 90             | Pro-R          |
| C(11)  | N(12)     | 1.438           | Mn(25)         | 104                | N(4)          | 63.433         | Dihedral       |
| C(19)  | N(20)     | 1.438           | Mn(25)         | 104                | N(4)          | 127.21         | Dihedral       |
| C(5)   | N(4)      | 1.438           | C(3)           | 104                | Mn(25)        | 109.5          | Pro-S          |
| O(7)   | Mn(25)    | 1.81            | N(4)           | 90                 | N(12)         | 90             | Pro-S          |
| C(13)  | N(12)     | 1.438           | C(11)          | 104                | Mn(25)        | 109.5          | Pro-R          |
| O(15)  | Mn(25)    | 1.81            | N(4)           | 90                 | O(7)          | 90             | Pro-R          |
| C(21)  | N(20)     | 1.438           | C(19)          | 104                | Mn(25)        | 109.5          | Pro-R          |
| O(23)  | Mn(25)    | 1.81            | N(4)           | 90                 | O(7)          | 90             | Pro-R          |
| C(6)   | C(3)      | 1.509           | N(4)           | 104                | C(5)          | -179.161       | Dihedral       |
| C(2)   | C(3)      | 1.523           | N(4)           | 104                | C(6)          | 107.8          | Pro-S          |
| C(14)  | C(11)     | 1.509           | N(12)          | 104                | C(13)         | 154.66         | Dihedral       |
| C(10)  | C(11)     | 1.523           | N(12)          | 104                | C(14)         | 107.8          | Pro-R          |
| C(22)  | C(19)     | 1.509           | N(20)          | 104                | C(21)         | 179.973        | Dihedral       |
3.2 Conductivity analysis

The equivalent conductivity ($\Lambda_{\text{equiv}}$) at each concentration of each electrolyte solution was calculated by the following equation:

$$\Lambda_{\text{equiv}} = \frac{1000\sigma}{C_1C_2}$$

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[24]. Table 2a, 2b, and 2c shows the values of the equivalent conductivity and concentrations of the two electrolytes salts (2:1) determined experimentally. The Kohlrausch equations was used to discover types of electrolyte through plot the relation between equivalent conductivity against the square root of concentration [25] at different temperature (288.16 -313.16 K) and different solvent (water, methanol, and their mixtures) as shown in the Figures 2a, 2b and 2c.

| C(18) | C(19) | 1.523 | N(20) | 104         | C(22) | 107.8 | Pro-R  |
| C(1)  | C(5)  | 1.951 | N(4)  | 90.278     | C(3)  | 53.812 | Dihedral |
| C(9)  | C(13) | 1.523 | N(12) | 104        | C(11) | -41.253 | Dihedral |
| C(17) | C(21) | 1.523 | N(20) | 104        | C(19) | -40.289 | Dihedral |
| O(8)  | C(6)  | 1.208 | C(3)  | 131.989    | O(7)  | 131.989 | Pro-S  |
| O(16) | C(14) | 1.208 | C(11) | 161.472    | O(15) | 161.472 | Pro-R  |
| O(24) | C(22) | 1.208 | C(19) | 131.694    | O(23) | 131.694 | Pro-R  |
| H(30) | C(3)  | 1.113 | C(2)  | 112.303    | N(4)  | 115.659 | Pro-R  |
| H(37) | C(11) | 1.113 | C(10) | 112.303    | N(12) | 115.659 | Pro-S  |
| H(44) | C(19) | 1.113 | C(18) | 112.303    | N(20) | 115.659 | Pro-S  |
| H(26) | C(1)  | 1.113 | C(2)  | 111.843    | C(5)  | 111.843 | Pro-R  |
| H(27) | C(1)  | 1.113 | C(2)  | 115.113    | C(5)  | 115.113 | Pro-S  |
| H(28) | C(2)  | 1.113 | C(1)  | 110.797    | C(3)  | 110.797 | Pro-R  |
| H(29) | C(2)  | 1.113 | C(1)  | 112.642    | C(3)  | 112.642 | Pro-S  |
| H(31) | C(5)  | 1.113 | C(1)  | 114.005    | N(4)  | 114.005 | Pro-R  |
| H(32) | C(5)  | 1.113 | C(1)  | 120.26     | N(4)  | 120.26  | Pro-S  |
| H(33) | C(9)  | 1.113 | C(10) | 110.543    | C(13) | 110.543 | Pro-S  |
| H(34) | C(9)  | 1.113 | C(10) | 112.043    | C(13) | 112.043 | Pro-R  |
| H(35) | C(10) | 1.113 | C(9)  | 110.641    | C(11) | 110.641 | Pro-S  |
| H(36) | C(10) | 1.113 | C(9)  | 112.275    | C(11) | 112.275 | Pro-R  |
| H(38) | C(13) | 1.113 | C(9)  | 110.797    | N(12) | 110.797 | Pro-S  |
| H(39) | C(13) | 1.113 | C(9)  | 112.642    | N(12) | 112.642 | Pro-R  |
| H(40) | C(17) | 1.113 | C(18) | 111.147    | C(21) | 111.147 | Pro-S  |
| H(41) | C(17) | 1.113 | C(18) | 113.468    | C(21) | 113.468 | Pro-R  |
| H(42) | C(18) | 1.113 | C(17) | 114.708    | C(19) | 114.708 | Pro-S  |
| H(43) | C(18) | 1.113 | C(17) | 121.948    | C(19) | 121.948 | Pro-R  |
| H(45) | C(21) | 1.113 | C(17) | 110.797    | N(20) | 110.797 | Pro-S  |

...
Table 2a. Molar concentration (M) and Equivalent conductance of [Mn(pro)₃]Cl₂ in water at different temperatures

| Conc. Mole/L *10⁻⁷ | √Conc. (mole/L) *10⁻⁴ | Λ (Ohm⁻¹, equiv⁻¹ cm²) 288.16 K | Λ (Ohm⁻¹, equiv⁻¹ cm²) 293.16 K | Λ (Ohm⁻¹, equiv⁻¹ cm²) 298.16 K | Λ (Ohm⁻¹, equiv⁻¹ cm²) 303.16 K | Λ (Ohm⁻¹, equiv⁻¹ cm²) 308.16 K | Λ (Ohm⁻¹, equiv⁻¹ cm²) 313.16 K |
|-------------------|------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 2.5643            | 7.1990                 | 194.9821                      | 210.0046                     | 195.0748                     | 192.9125                     | 257.3206                     | 189.5213                     |
| 5.0213            | 10.2689                | 165.9666                      | 190.9497                     | 190.9014                     | 164.2526                     | 230.0771                     | 184.239                      |
| 7.5435            | 12.5406                | 154.5371                      | 185.9497                     | 173.0658                     | 152.9858                     | 196.8279                     | 172.8288                     |
| 9.8325            | 14.3921                | 152.4805                      | 177.9343                     | 166.0891                     | 150.9934                     | 184.6956                     | 166.3414                     |
| 12.2964           | 16.0571                | 149.0946                      | 170.0499                     | 159.5157                     | 147.6829                     | 174.6973                     | 160.2151                     |
| 14.7457           | 17.4490                | 147.4802                      | 168.6692                     | 144.1688                     | 146.1662                     | 168.166                      | 156.3808                     |
| 16.9542           | 18.6958                | 147.0327                      | 169.5794                     | 135.1085                     | 145.589                      | 165.8528                     | 150.961                      |
| 19.2708           | 20.0543                | 146.9388                      | 165.0565                     | 127.3933                     | 137.1891                     | 163.1273                     | 149.8349                     |
| 21.5852           | 21.1831                | 146.9516                      | 162.1295                     | 126.3367                     | 130.1396                     | 158.3273                     | 146.3369                     |
| 23.8737           | 22.3235                | 146.6762                      | 161.2595                     | 125.9081                     | 129.9399                     | 155.9928                     | 140.0646                     |
| 26.2474           | 23.2902                | 146.0461                      | 160.3251                     | 122.3702                     | 128.704                      | 153.8403                     | 133.8626                     |
| 28.2739           | 24.3409                | 141.4737                      | 157.021                      | 120.1549                     | 127.0049                     | 149.8012                     | 130.5831                     |
| 30.4031           | 25.2974                | 140.0465                      | 151.9279                     | 120.873                      | 124.2806                     | 148.8608                     | 127.3397                     |
| 32.6374           | 26.1169                | 139.6655                      | 150.9272                     | 120.4697                     | 121.4671                     | 146.9295                     | 124.0498                     |

Figure 2a. The relation between the square root of concentration and the equivalent conductance of [Mn(pro)₃]Cl₂ in water at different temperatures.
**Table 2b.** Molar concentration (M) and Equivalent conductance of \([\text{Mn(pro)}_3]\text{Cl}_2\) in methanol at different temperatures

| Conc. Mole/L *10\(^{-7}\) | √Conc. (mole/L) *10\(^{-4}\) | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 288.16 K | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 293.16 K | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 298.16 K | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 303.16 K | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 308.16 K | \(\Lambda\) (Ohm\(^{-1}\), equive\(^{-1}\), cm\(^2\)) 313.16 K |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 6.55604         | 8.0969          | 77.7410         | 77.5926         | 74.4429         | 75.5798         | 76.1726         | 78.6841         |
| 12.8632         | 11.3416         | 76.2651         | 77.2447         | 74.0047         | 64.2040         | 64.7040         | 76.1726         |
| 19.3808         | 13.9215         | 68.7964         | 76.1236         | 66.7687         | 59.6598         | 60.1211         | 69.6153         |
| 25.3026         | 15.9068         | 65.8691         | 65.7373         | 63.9330         | 58.7554         | 52.6280         | 66.6383         |
| 31.6924         | 17.8023         | 63.1065         | 62.9772         | 61.2569         | 57.3355         | 47.2685         | 63.8290         |
| 38.0817         | 19.5145         | 61.2716         | 61.1434         | 59.4811         | 56.9934         | 43.7078         | 57.5337         |
| 43.8606         | 20.9429         | 60.7986         | 60.6685         | 59.0265         | 56.4978         | 41.7432         | 53.7839         |
| 49.9570         | 22.3510         | 60.0514         | 59.9202         | 58.3060         | 52.9118         | 39.9800         | 50.5822         |
| 56.0792         | 23.6810         | 59.4396         | 59.3069         | 57.7168         | 50.0831         | 38.5826         | 48.0535         |
| 61.9826         | 24.8963         | 56.4674         | 59.0214         | 57.4462         | 47.9801         | 37.5924         | 46.1840         |
| 68.4457         | 26.1621         | 53.5704         | 53.3046         | 56.7561         | 45.8649         | 36.4736         | 44.2733         |
| 73.8580         | 27.1768         | 51.9013         | 58.5320         | 56.9842         | 44.7424         | 36.0535         | 43.2991         |
| 79.5650         | 28.2072         | 50.2732         | 56.4208         | 54.9356         | 43.6111         | 35.5585         | 42.2996         |
| 85.6442         | 29.2650         | 48.6508         | 54.3548         | 52.9308         | 42.4462         | 34.9770         | 41.2530         |

**Figure 2b.** The relation between the square root of concentration and the equivalent conductance of \([\text{Mn(pro)}_3]\text{Cl}_2\) in methanol at different temperatures
Table 2c. Molar concentration (M) and Equivalent conductance of [Mn(pro)$_3$]Cl$_2$ at different percentage of methanol in water

| Conc. (Mole/L) $\times 10^{-7}$ | $\sqrt{\text{Conc. (mole/L)}}$ $\times 10^{-4}$ | $\Lambda$ (Ohm$^{-1}$. equiv$^{-1}$. cm$^2$) 10% | $\Lambda$ (Ohm$^{-1}$. equiv$^{-1}$. cm$^2$) 20% | $\Lambda$ (Ohm$^{-1}$. equiv$^{-1}$. cm$^2$) 30% | $\Lambda$ (Ohm$^{-1}$. equiv$^{-1}$. cm$^2$) 40% | $\Lambda$ (Ohm$^{-1}$. equiv$^{-1}$. cm$^2$) 50% |
|--------------------------------|-------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| 2.6646                         | 5.1620                                          | 375.2790                                       | 258.8416                                       | 244.8986                                       | 234.5255                                       | 239.1073                                       |
| 5.2282                         | 7.2308                                          | 286.8876                                       | 230.8790                                       | 208.7791                                       | 186.9101                                       | 182.7888                                       |
| 7.8743                         | 8.8760                                          | 253.8579                                       | 197.0221                                       | 184.6778                                       | 165.3729                                       | 161.7446                                       |
| 10.2086                        | 10.1419                                         | 226.8457                                       | 184.4627                                       | 176.7567                                       | 158.3136                                       | 154.8570                                       |
| 12.8855                        | 11.3510                                         | 206.9663                                       | 174.0534                                       | 169.2722                                       | 151.6546                                       | 148.3508                                       |
| 15.4832                        | 12.4431                                         | 193.7569                                       | 155.9976                                       | 146.2815                                       | 127.0949                                       | 123.7389                                       |
| 17.8329                        | 13.3541                                         | 186.9163                                       | 145.1320                                       | 126.9573                                       | 105.6531                                       | 100.0464                                       |
| 20.1315                        | 14.2524                                         | 180.5070                                       | 135.9232                                       | 120.8390                                       | 104.4238                                       | 97.6217                                        |
| 22.8384                        | 15.1009                                         | 175.4092                                       | 128.6584                                       | 115.2318                                       | 97.2413                                        | 91.7597                                        |
| 25.2536                        | 15.8761                                         | 171.9211                                       | 123.2607                                       | 113.9772                                       | 93.4384                                        | 87.4304                                        |
| 27.8625                        | 16.6841                                         | 167.6471                                       | 117.8233                                       | 106.8409                                       | 89.7613                                        | 83.7404                                        |
| 30.3722                        | 17.3312                                         | 160.9114                                       | 114.9500                                       | 102.8120                                       | 85.9980                                        | 79.7538                                        |
| 32.5904                        | 17.9886                                         | 154.5163                                       | 112.0496                                       | 100.8455                                       | 83.0980                                        | 77.4660                                        |
| 34.8368                        | 18.6637                                         | 148.3239                                       | 109.0573                                       | 98.8550                                        | 81.2680                                        | 74.4249                                        |

Figure 2c. The relation between the square root of concentration and Equivalent conductance of [Mn(pro)$_3$]Cl$_2$ at different percentage of methanol in water

Figures 2a and 2b show the relations between ($\Lambda$) and concentration ($\sqrt{c}$) for the studied complex at different temperatures. Gave a curved line, these relationships which indicate that complex of amino acid was weakly associated in different solvents and temperatures [26]. Moreover, Figure 2c shows the relation between ($\Lambda$) and the square root of concentration ($\sqrt{c}$) for the studied complex at different percentages of methanol to water which also gave a curve line. The Lee-Wheaton equation (LW) for unsymmetrical electrolytes is used for analyses of the conductance data for mixed electrolyte solutions using a computer program (AM1).

The theoretical equivalent conductance is given by the following equation.

$$\Lambda_{equiv} = \Sigma |Z_i| \frac{\text{m}_i}{\Sigma \text{C}_n}$$

(2)

Where $Z_i$ is the charge, $\text{m}_i$: 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 \( K_a \) and \( \lambda^o_{s} \) value for single ion and for ion-pair are constant from one system to another for symmetrical, asymmetrical and mixed electrolytes by using LW equation\[27\].The input data of the computer program (AM1) are: solvent parameters (\( T, \ D, \ \eta \)), charges \( Z_i \) and limiting conductivities \( \lambda^o_i \) for each ionic species. \( K_{association} \) for each ion association equilibrium as shown in tables (3a, 3b and 3c); for mixture as an example and the experimental data which are the stoichiometric concentration of the two electrolytes solution within the experimentally determined equivalent conductivities calculated from equation (1). The computer program (AM1) calculated the minimum standard deviation \( \sigma(\Lambda) \) between \( \Lambda_{equiv} \) (found experimentally) using equation (1) and \( \Lambda_{equiv} \) (Calculated by using equation (2) as
\[
\sigma(\Lambda) = (\Lambda_{equiv} - \Lambda_{exp})^3 \ldots .(3)
\]
at the appropriate (\( R \)) values (\( R \): the overall distance parameter), where \( R \) is only the variable parameter, for each set of the data of each experiment done\[28\]. Tables 3a, 3b and, 3c show the results of proline complex analysis in water and methanol at different temperatures and at mixtures.

**Table 3a.** The values at constant \( K_a, \Lambda \),the distance between \( R(\Lambda^o) \) and \( \sigma\Lambda \) of the\([Mn(pro)_3]Cl_2\) at different temperatures in water solvent.

| \( T \)  (K) | \( K_a \) | \( \Lambda^o \) (Ohm\(^{-1}\).equiv\(^{-1}\).cm\(^2\)) | \( R \) (A\(^{°}\)) | \( \sigma\Lambda \) |
|-----------|-----|-----------------|--------|--------|
| 288.16    | 30  | 90              | 7.4    | 0.072  |
| 293.16    | 25  | 110             | 7.1    | 0.112  |
| 298.16    | 72  | 74              | 7.5    | 0.171  |
| 303.16    | 92  | 78              | 7.4    | 0.127  |
| 308.16    | 82  | 98              | 7.0    | 0.168  |
| 313.16    | 122 | 92              | 7.0    | 0.128  |

**Table 3b.** The values at constant \( K_a, \Lambda \),the distance between \( R(\Lambda^o) \) and \( \sigma\Lambda \) of the\([Mn(pro)_3]Cl_2\) at different temperatures in methanol solvent.

| \( T \)  (K) | \( K_a \) | \( \Lambda^o \) (Ohm\(^{-1}\).equiv\(^{-1}\).cm\(^2\)) | \( R \) (A\(^{°}\)) | \( \sigma\Lambda \) |
|-----------|-----|-----------------|--------|--------|
| 288.16    | 6   | 18              | 5.4    | 0.07   |
| 293.16    | 10  | 15              | 5.8    | 0.061  |
| 298.16    | 10  | 12              | 4.5    | 0.057  |
| 303.16    | 8   | 11              | 5.2    | 0.085  |
| 308.16    | 6   | 10              | 5      | 0.151  |
| 313.16    | 4   | 6               | 5.9    | 0.102  |

**Table 3c.** The values at constant \( K_a, \Lambda \),the distance between \( R(\Lambda^o) \) and \( \sigma\Lambda \) of the\([Mn(pro)_3]Cl_2\) in different percentage of methanol in water.

| \%      | \( K_a \) | \( \Lambda^o \) (Ohm\(^{-1}\).equiv\(^{-1}\).cm\(^2\)) | \( R \) (A\(^{°}\)) | \( \sigma\Lambda \) |
|---------|-----|-----------------|--------|--------|
| 10      | 52  | 122             | 5.5    | 0.209  |
| 20      | 71  | 120             | 7.9    | 0.21   |
| 30      | 92  | 91              | 7.2    | 0.161  |
| 40      | 110 | 82              | 8.1    | 0.112  |
| 50      | 132 | 62              | 8.2    | 0.169  |
It is noted that the Ka values of complex increase with increasing temperature because the electronic density of the solvent decrease, associations will decrease 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 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 increased temperatures [29]. The values of σΛ give an indication of good best-fit values [30].

3.3 Calculation of the thermodynamic parameters (ΔH, ΔG, ΔS)
Thermodynamic functions of proline complex were estimated through the value of the equilibrium constant at different temperatures by the Vant-Hoff equation. ΔH values were calculated from the relation between lnKa against 1/T as shown in Figures 3a and 3b. The relation gives a straight line for complex solutions [31].

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

While ΔS values were calculated from the equation:

\[
\Delta G = \Delta H - T \Delta S
\]  

and ΔG from the equation:

\[
\Delta G = -RT \ln Ka
\]  

The values of thermodynamic parameters (ΔH, ΔG, ΔS) shows in Table (4a and 4b)

| T (K) | ΔS (J.mol⁻¹.K⁻¹) | ΔG (KJ.mol⁻¹) | ΔH (KJ.mol⁻¹) | Ln ka |
|-------|-----------------|---------------|---------------|-------|
| 288.16 | 28.26           | -8.1444       | -5.59         | 3.401 |
| 293.16 | 26.74           | -7.84163      | 3.219         |
| 298.16 | 35.54           | -10.5963      | 4.277         |
| 303.16 | 37.58           | -11.3917      | 4.522         |
| 308.16 | 36.62           | -11.2850      | 4.407         |
| 313.16 | 39.93           | -12.5021      | 4.804         |

Table 4a. Thermodynamic parameters of [Mn(pro)₃]Cl₂ in water.
Figure 3a. The relation between the ln Ka & 1/T of [Mn(pro)$_3$]Cl$_2$ in water.

Table 4b. Thermodynamic parameters of [Mn(pro)$_3$]Cl$_2$ in methanol.

| T (K)  | ΔS (J.mol$^{-1}$.K$^{-1}$) | ΔG (KJ.mol$^{-1}$) | ΔH (KJ.mol$^{-1}$) | ln ka |
|------|-----------------|--------------|-----------------|--------|
| 288.16 | 28.8            | -8.299       | -3.41           | 3.466  |
| 293.16 | 31.26           | -9.163       | -4.159          | 3.761  |
| 298.16 | 32.68           | -9.742       | -4.431          | 3.932  |
| 303.16 | 34.57           | -10.48       | -4.961          | 4.159  |
| 308.16 | 35.55           | -10.95       | -5.777          | 4.277  |
| 313.16 | 36.83           | -11.53       | -6.694          | 4.431  |

Figure 3b. The relation between the ln Ka & 1/T of [Mn(pro)$_3$]Cl$_2$ in methanol.

The values of ΔH (enthalpy of association) were negative(exothermic) which show that the operation was hydration, while ΔG (Gibbs free energy) had negative values which depend upon the kind of ions and in agreement with the relation, which means that the reaction was spontaneous towards the association and the values of ΔS were also positive (increase the random with increase the temperature) [32].

3.4 Statistical analysis
After completing the analysis of conductivity results and determining the Ka and R, the statistical analysis used to find the relationship between the parameters by suggesting an intensive model that is nearly close to accurate mathematical methods with excellent regression parameters. Thus, the first descriptor was selected in accordance with the simple correlation between the Ka and the adjusted parameters as exhibited in Table 5. Below the model equation (eq.7), which was obtained by multiple
linear regression, with $r^2$ and $q^2$ equal to 0.999 and 0.994 respectively. The suggested model can be used to predict the $K_a$ value from the dielectric constant and viscosity of solvents before experiments.

$$K_a = 531 - 0.6 \text{ dielectric const.} - 65472 \text{ Viscosity}$$  \hspace{1cm} (7)

| % MeOH | Ka | Viscosity (Poise) | Density (g/cm$^3$) | Dielectric Const. | $R$ (Å$^0$) | $\Lambda^0$ (Ohm$^{-1}$, equiv$^{-1}$, cm$^2$) |
|-------|-----|-------------------|-------------------|-------------------|-------------|----------------------------------|
| 10    | 52  | 0.00664           | 0.9737            | 69.64             | 5.5         | 122                               |
| 20    | 71  | 0.00638           | 0.9534            | 65.2              | 7.9         | 120                               |
| 30    | 92  | 0.00612           | 0.9331            | 60.8              | 7.2         | 91                                |
| 40    | 110 | 0.00586           | 0.9128            | 56.418            | 8.1         | 82                                |
| 50    | 132 | 0.0056            | 0.8925            | 52                | 8.2         | 62                                |

| Obs   | $K_a$ experimentaly | $K_a$ theoretically |
|-------|---------------------|---------------------|
| Training set |
| 1     | 52                  | 51.647              |
| 2     | 71                  | 71.065              |
| 3     | 110                 | 111.213             |
| 4     | 132                 | 131.075             |
| Test set |
| 5     | 92                  | 93.83               |

4. Conclusions:
The present work reports conductivity data for proline-Mn solutions in water, methanol at different temperatures and in mixtures of methanol in water, which were measured by assisting the lee-Wheaton equation at the best fit values of standard deviled ($\sigma A$) for analyzing the data of unsymmetrical electrolytes included. The values of conductivity parameters such as association constant $K_a$, $\Lambda_0$, and distance parameter $R$, were differ from one solvent to another depending on dielectric constant and viscosity and interactions in solution. An indication of the above can be said that the electrophoretic effect or asymmetric effect. The Affected $K_a$ values were in the following order [mixture> methanol> water], due to the difference in the density, viscosity and, dielectric constant which decreases with the increase of alcohol content. Consequently, increased intermolecular interaction and ionic hydration between the methanol and water molecules are responsible for the decrease in density which is in coherence with the available literature values. Therefore, the mixture results are better than those of methanol or water alone. Also, from theoretical results, the effect of the solvent property upon the $K_a$ is in matching with the experimental results.

5. Acknowledgments
The authors are very grateful to the University of Mosul / College of Science, for their provided facilities, which helped to improve the quality of this work.

References
[1] Lu J, Meng D, Li F, Guo M and Li Y 2020 Russ. J. Phys. Chem. A, 94 1427.
[2] Lahsasni S A, Ammar R A and Amin M F INT J ELECTROCHEM SC, 7 7699.
[3] Sigel H, Opserschall B P, Massoud S S, Song B and Griesser R 2006 Dalton Transactions, 46 5521.
[4] Udhayakumar S, Shankar K G, Sowndarya S, Venkatesh S, Muralidharan C and Rose C 2017 RSC Advances, 7 25070.
[5] Datta P K, Chandra M and Dey A K 1980 Transition Metal Chemistry, 5 1.
[6] Long D , Wilkinson K L , Poole K, Taylor D K , Warren T, Astorga A M and Jiranek V 2012 J. Agric. Food Chem., 60 4259. 
[7] Abrahám E , Hortón-Cabassa C, Erdei L and Szabados L Methods Mol Biol., 639 317. 
[8] Lü Z, Zhang H, Zhang Y, Guan Y J and Chengyin W 2016 JCS. 54(10) 1743. 
[9] Costín J W , Barnett N W and Lewis S W 2004 Talanta. 64(4) 894. 
[10] Kurtiz A F , Boynton A W , David G A, Colyer K E and Poutsma J C 2002 JASMS, 13(1) 72. 
[11] Domínguez M A , Jacksén J, Emmer Å and Centurión M E 2016 Microchemical Journal, 129 1. 
[12] Wang Y, Shang Z C, Wu T X, Fan J C and Chen X 2006 J Mol Catal A Chem. 253 ( 1-2) 212. 
[13] Huang X Y, Wang H J and Shi J 2010 J. Phys. Chem. A,114(2) 1068. 
[14] Al-Healy F and Hamed Y 2019 EPSTEM . 7 48. 
[15] Al-Allaf Y O , Al-Tamer M Y and Abdul fattah M N Raf.J.Sci.24 45. 
[16] Petruhina V A , Kurnaleva T A, Egorova D A and Koltsov N I 2016 Butlerov Communications.45 107. 
[17] Petruhina V A , Kirillova T A , Tcareva L Y, Andreeva E V and Koltsov N I 2019 Butlerov Communications.57 54. 
[18] Wagner H 2012 Power Plant Chemistry,14 455. 
[19] Bøskov p., Sokol v., Tomaš R and Prkic A Int. J. Electrochem. Sci., 8 10961. 
[20] Itte P, Amshumali M K and Mussavir P K M 2017 Univers. J. Chem.5 48. 
[21] Hummodat M Z and Mustafa I 2013 Synthesis and Characterization of Mixed ligand Complexes of Nickal(II) Copper(II) Palladium(II) Platinum(IV) and Gold(II) with Some Amino Acid and Dithiocarbamates or Dithiophosphat in Thetriphenylphosphine Adducts with some of the Nickal(II) Complexes , Ph.D., University of Mosul,College of Science. 
[22] Palmer, W.G. (1954). Experimental Physical Chemistry. (Cambridge at the University Press, London) 186. 
[23] Abdulrahman S H and Khalil R A 2020 Statistical Treatment for study the Relationship between the Chemical Structure and Activity of some biologically Active Isatin Derivatives Using Quantum Mechanics Methods, Ph.D., University of Mosul ,College of Science. 
[24] Akrawi B A, Al-Nuri I J and Khalil S M 1991 Iraqi J.Chem.16 67. 
[25] Lee W H and Wheaton R J 1978 J.C.S.Faraday II., 74, pp.743. 
[26] AL-Bashar M.N., Jamil A. M.; (2016), “Determination of Thermodynamic Functions for Ion Association of Hippuric Acid in 20% Aqueous Ethanol” Res. J. Chem. Sci., 6, No.2, pp.15. 
[27] Lee, W.H.; Wheaton, R.H. (1979). The conductivity of dilute aqueous solutions of magnesium chloride at 25°C. J. Chem. Soc., Faraday II,75 1128. 
[28] Akrawi B A and Haneed Y O 2005 .IASS. 16 165. 
[29] Radhika V and Manikyamba P 2008 . Indian J. Chem. 47[A] 1814. 
[30] Al-Alalf Y O , Ahmed S A and Ahmed,R.H Raf.J.Sci. 27 58. 
[31] Edders D F , Gregory N W , Halsey G D , Rabinovitch B S 1964 Physical Chemistry,( John Wiley and Sons, Inc. New York) p. 198 
[32] Robert G M 2008 Physical Chemistry. 3rd ed., (Elsevier Inc., Burlington, USA) p 1. 

12