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DFT Analysis of Ions Conductivity of Proline in Certain Solvents: Calculation of Association Parameters

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Abstract: Proline (Pro.) is non-essential amino acid, and it is from the amino acids which the human's body can synthesize it, from L-glutamate. It is studied in the temp. range from 288.16 to 313.16 K at 5 K by conductivities in H_2O, and methanol. The Kohlrausch equations was used to find out pattern of electrolyte, the curve indicate pro. was weakly associated in various temperatures and solvents. The Lee-Wheaton equation was us to calculation the Equivalent conductance at infinite dilution (Λo), The association constant (Ka) and distance parameter (R). The values of (Λo), (Ka), and (R) differ from solvent to another depending on the interactions in solution. The molecular modeling, geometry optimization and characterization of pro. has been performed using semi empirical method, and all theoretical parameters was calculated by using Austin Model 1 (AM1), and used density functional theory (DFT) B3LYP method by using 6-311G bases set.

Keywords: Proline, Kohlrausch equations, Lee-Wheaton equation, AM1, DFT

Introduction

Proline, which is an amino acid, in fact is one of the twenty amino acids found most frequently in animal proteins. Only the L version (L-prol.) may be found in mammalian proteins. It is not an essential amino acid because it can be produced in the human body. İt is one of the most popular in the cellular milieu, accounting for roughly 25% of residues in collagen, the primary protein in the extracellular matrix, along with hydroxyproline (Liu et. al., 2012).

Using a literature search, we discovered numerous previously published methods for determining pro. in biological fluids. Pro. in human serum detection using a robust LC-MS/MS which is a classic method for determining it in human serum (Su et. al., 2015). Other methods were developed employing Fluorometric measurement of pro. in honey by high-performance liquid chromatography after pre-column derivatization with 7-fluoro-4-nitrobenzo-2-oxa-1,3-diazole (NBD-F), with a detection limit of 3.00 mg kg1 and recoveries of more than 90%. (Li et. al., 2015). Amino acid and antioxidant installation of three medicinal plants from the uttarakhand himalayas (Pithoragarh). Also the simultaneous analysis of 26 physiological amino acids in plasma along with total cysteine and homocysteine by high-performance liquid chromatography (HPLC) employing 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) as precolumn derivatizing reagent (Gaurav et. al., 2014). The equivalent conductivities of pro-Mn (II) Complex in H_2O, MeOH, and mixes of MeOH and water at proportions from hundreds of 10, 20, 30, 40, and 50 of MeOH were examined at 310.16K in the temperature range of 288.16 to 313.16 K at 5 K intervals (Al-Healy et. al., 2021). LiClO4 in propylenecarbonate is a nonassociated electrolyte, according to the Lee-Wheaton equation of conductivity. The results of conductometric examinations of solutions of numerous 1-1 electrolytes in propylene carbonate at temperatures ranging from 298 to 398 K are reported to account for the dynamics of ionic solvation (Chernozhak, et. al., 2016)

The electrical conductivities of tyrosine in aqueous solutions was measured by using Kohlrausch equation and Lee-Wheaton equation at 310.16K then They prepared complexes of tyrosine with Co(II) , Mn(II) , Ni(II) , Fe(II) , to form $[Ni(tyr)_3]Cl_2$, $[Co(tyr)_3]Cl_2$, $[Fe(tyr)_3]Cl_2$, $[Mn(tyr)_3]Cl_2$ this complexes are measured using in the temperature range from (288.16–313.16K) from the conductivity result they calculation of the thermodynamic quantities (ΔH°, ΔG°, ΔS°) (Al-Healy et. al., 2019). The electrical conductivities of glutamic acid in the water, MeOH, and EtOH are measured at 310.16 K and the main interest is to find an accurate yet efficient solvation model for semiempirical quantum-mechanical and Density Function Theory (DFT) methods applicable to amino acids (glutamic acid) in the context of computer-aided conductivity studying (Abdulrahmana et. al., 2021).

Kohlrausch equations was used to discover types of electrolyte through plot the relation between equivalent conductivity against the square root of molar concentration of pro. The plot indicate that amino acid was weakly associated in water and MeOH (Al-Healy et. al., 2021). In the domains of chemical, biological, and material sciences, computational chemistry is becoming increasingly relevant. (Mourik, et. al., 2012). It aids in the knowledge of molecular structure in organic chemistry, providing insight into reaction pathways and chemical reactions through the assessment of geometrical features of molecules. (Art et. al., 2016; Miriding et. al., 2017).

Conceptual Density Functional Theory (DFT) or Chemical Reactivity Theory (as it is also known) is a strong tool for predicting, analysing, and interpreting the outcome of chemical interactions. In this study, a series of molecular descriptors and attributes of their optimal geometries were calculated using density functional theory (DFT) and thermodynamics modelling (Dehdab et al, 2016). Theoretical studies provide insights into this kind of study in conductivity and have been making a great contribution to support experimental results. Comparing experimental results and theoretical studies indicates that some density functional theory calculations (DFT) consistently underestimate band gaps (Lu et al, 2019).

Experimental Methodology

Computational Details

All calculations were done with the Gaussian '09 program package and semi-empirical methods. Semi-empirical approaches are based on what is commonly referred to as empirical methods. After energy minimization and geometry optimization, the DFT approach was utilized with the hybrid B3LYP model (Becke's three-parameter hybrid exchange functional with the Lee-Yang–Parr correlation functional) and basis set 6-311G for equilibrium geometry at ground state in water and MeOH. The properties of the thermodynamic, electronic, and other descriptors were calculated.

Expermental Details

For measuring the conductance of the fluids, a general approach was utilized in which the conductivity cell was cleaned, dried, weighed empty, and kept at a constant temperature (0.1oC) using a water circulation ultra thermostat. The conductivity of the sample was observed using a WTW Inolab 740 computerized conductometer after a particular amount of solution was introduced into the conductivity cell. A 1ml syringe was used to inject another known volume of fluid, and the measurement was repeated. By weighing the amount for each one, approximately (15) additions have been made.

Results and Discussion

The relationship between equivalent conductivity and the square root of the molar concentration of pro. was shown using Kohlrausch equations to identify types of electrolytes. The amino acid was poorly linked in water and MeOH, according to the plot which had from the results. The pro. solution promised symmetrical electrolytes of type (1:1) if the positive ion is denoted by (M+) and negative ion (X-) when using the equation for these solution can be explaining as follows (Al-Healy et. al., 2019).

$$M + aq. + X\text{-}aq \rightarrow . Ka \rightarrow (M.aq + n\ X)$$

Ka: association constant K

Figure (1) demonstrates this behavior

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

Conc.*10^{-7} M	√Conc. *10^{3} M	Λ (Ohm^{-1}. $equive^{-1}$ .cm^{2})
5.2573	0.6609	142.6582
10.2259	0.9096	97.79028
14.9181	1.1019	83.79053
19.9200	1.2654	75.30096
24.6343	1.4150	71.03902
29.6084	1.5435	67.54828
34.2994	1.6665	58.30994
39.1146	1.7941	51.13183
43.6948	1.8976	46.64819
48.2334	1.9816	45.77197

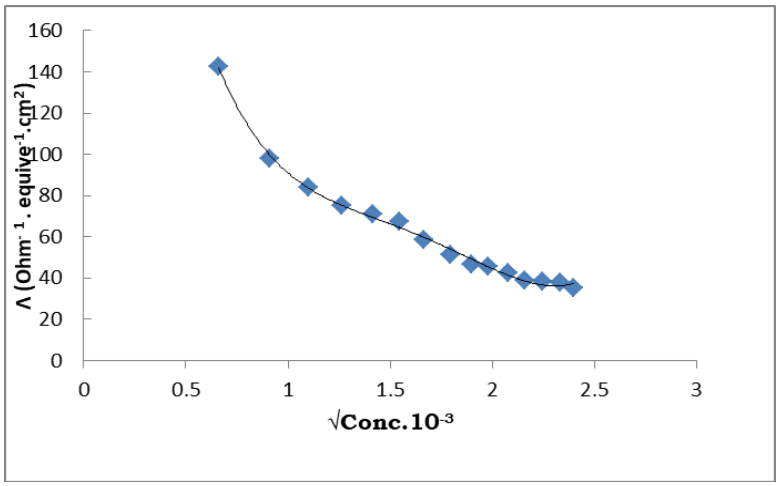


Figure 1. Equivalent conductance of Proline in water at 310.16K

Table 2. Molar concentration (M) and Equivalent conductance of Proline in methanol at 310.16K

Conc.*10^{-7} M	√Conc. *10^{3} M	Λ (Ohm^{-1}. $equive^{-1}$ .cm^{2})
5.3767	0.6609	92.9926
10.5242	0.9096	47.5091
15.2765	1.1019	32.7300
20.0511	1.2654	24.9362
24.8952	1.4150	20.0841
29.8601	1.5435	16.7447
34.6992	1.6665	15.4051
39.2040	1.7941	14.4095
44.4990	1.8976	14.0208
48.6850	1.9816	12.9178

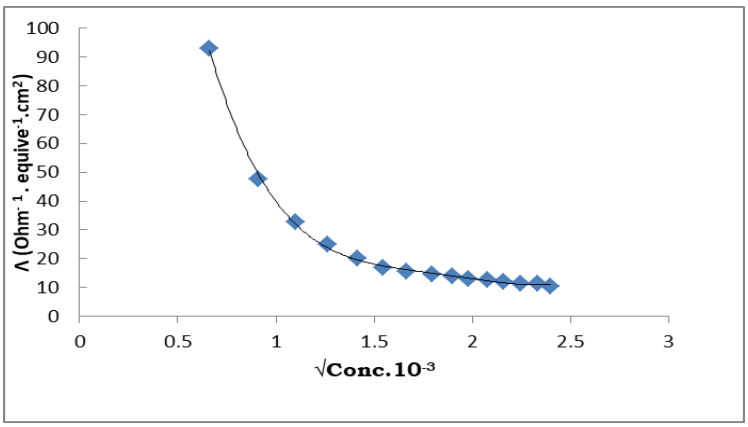


Figure 2. Equivalent conductance of Proline in methanol at 310.16K

The Lee-Wheaton equation is applicable to complete analysis of any sample symmetrical and asymmetrical electrolyte at different temperatures. the intent used is then to calculated the equivalent concentration for pro. 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 conc. of the pro. solution versus the equivalent continuation calculated through the calculation program(Al-Healy et. al., 2019). Figure (1) demonstrates this behavior.

Tables (3) show the results of the analysis complexes at different temperatures. where each table show the association constant (KA) and the equivalent conductance (Λ), the(R) values (distance parameter) and the best fit data standard deviation σs(Λ).

Table 3. Ka, Λ, R and σΛ of Proline in water and methanol

Solvents	Ka	Λ	R(A°)	бΛ
Water	10.6	379.6	$1*10^{-6}$	5.358
Methanol	49.73	110.012	$1*10^{-6}$	16.309

Optimizing of Molecular Geometry

The goal of geome optimization was to discover the optimal atomic arrangement that would make the molecule more stable. Topo-geometrical properties of the pro. molecule, such as bond lengths, bond angles, and dihedral angles, were optimized using semi-empirical approaches and subsequently DFT. Figure 3 shows the optimized structures of Iron bimetallic complexes with atom and number labeling.

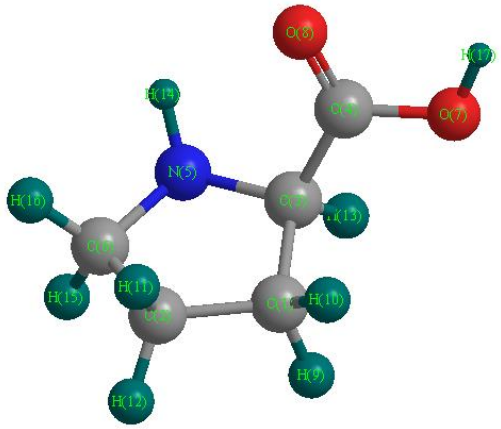
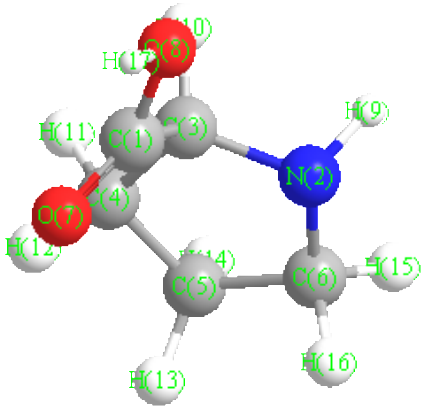
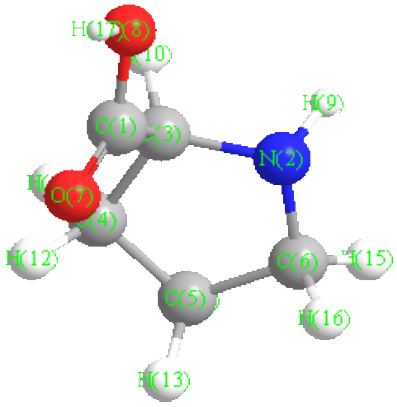


Figure 3. 3D-structure of Proline

Table 4: The 3D structures of Proline molecule in water and methanol by different approach

Type of Approach	Water	Methanol
AM1		
	Finished Energy = -98.19 Kcal/Mol	Finished Energy = -103.92 Kcal/Mol

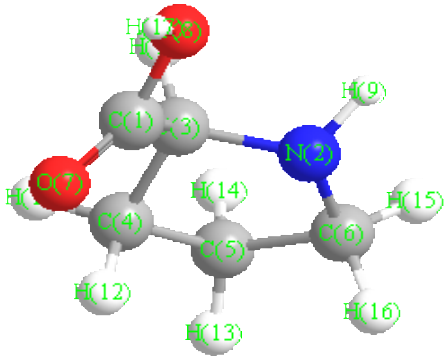
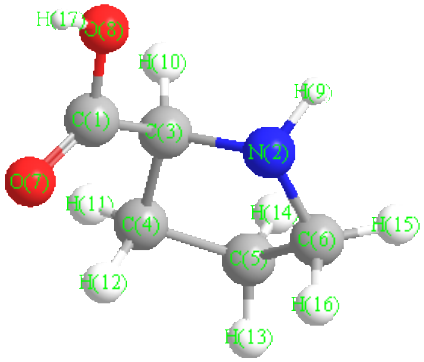
DFT (6-311G)		
	Finished Energy = -250171.43 Kcal/Mol	Finished Energy = -250119.79 Kcal/Mol

Table 5 shows the HOMO and LUMO orbital energies (in eV), as well as other descriptors. We formerly prepared many descriptors that tie the results acquired by HOMO and LUMO calculations to the experimental data.

Table 5: Parameters of Proline molecule in water and methanol were calculated by DFT method

Parameters	Water	Methanol
HOMO (eV)	-0.37843	-0.3648
LUMO (eV)	0.14339	0.1470
Gap (eV)	-0.52182	-0.5119
RMS Force: Kcal/Mole	0.0017	0.0035
SCF Energy: Kcal/Mole	-250290.11	-250288.96
Connolly Accessible Area: $(A°)^2$	277.449	272.687
Connolly Molecular Area: $(A°)^2$	126.886	123.486
Connolly Solvent Excluded Volume: $(A°)^3$	100.075	98.926
Dipole: Debye	1.8993	2.3779
Molecular Volume: bohr**3/mol	1025.511	915.473
Entropy: Cal/Mol-Kelvin	80.699	77.266
Thermodynamic Energy: Kcal/Mol	100.48	101.782
Zero-Point Energy: Kcal/Mol	96.889564	98.2333

The values of HOMO and LUMO were in a small deferent between them in MeOH and water. From the energies values the molecule of pro. is stable in the water than the MeOH, and the volume of space bounded by the solvent accessible molecular surface, which is Connolly Solvent Excluded Volume that refer to the volume in the water bigger than in the MeOH, in addition the Molecular Volume have the same indicators. Also the entropy value (S) in water more than in MeOH, which shows that the pro. molecule has more freedom of movement in water than MeOH and this is confirmed by the practical results through the value of the equivalent conduction in water is higher than in MeOH.

Conclusion

The calculations were made on the most stable conformer, after geometry optimizations, then compare the theoretical result with the experimental results which is in a similar evaluation that the conductivity of pro. in water more than MeOH. The molecular volume calculated by DFT analysis was big in the MeOH which has less mobility, which leads to a lower conductivity due to the lack of freedom of movement in the solution, and the reason is also due to the fact that the polarity of water and its dielectric constant is higher than MeOH.

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 dilution Λ° and the distance parameter R, which is very important constant in Thermodynamic.

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Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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