# Acoustic and Spectroscopic Study of L-Arginine Derivative in Non-Aqueous Medium

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Abstract- Solute solvent interactions are conveniently studied with application of acoustic and spectroscopy techniques. Measurement of sound velocity is having an important role in the study of thermodynamic properties such as internal pressure, free volume of solution. Different liquid systems differ essentially in their relative degree of cohesion. In the present study L. Arginine derivative in non-aqueous solution is taken as the sample and the fundamental parameters namely density, viscosity and ultrasonic velocity are determined for different concentrations from very low temperature to higher temperature. Using these fundamental quantities acoustic and thermodynamic parameters are computed and analyzed. The results obtained from spectroscopic and acoustic study support the significance of the thermodynamic behavior of the sample.

Keywords- Acoustic Study; Thermodynamic Behavior; Solute Solvent Interactions

### I. INTRODUCTION

Proteins are linear, large complex molecules, heterogeneous polymers genetically mandated with 20 different building blocks of all living organisms <sup>[1]</sup>. Amino acids and peptides are the fundamental structural units of proteins. Due to the complex nature of proteins, direct study is difficult <sup>[2]</sup>. In this work, ultrasonic study is carried out.

Ultrasonic study is a subject of extensive research and finds its usefulness in the field of biology, biochemistry, medicine, engineering, agricultural, field and industry <sup>[3]</sup>. The ultrasonic velocity along with other experimental data such as density and viscosity, furnish wealth of information about the interaction between ions, dipoles, hydrogen bonding, multipolar and dispersive forces <sup>[4, 5]</sup>. The study of the thermodynamic ability of the native structure of proteins has proved quite challenging one <sup>[6]</sup>.

Internal pressure gives an idea of the solubility characteristics. Free volume is one of the significant factors in explaining the variation in the physico-chemical properties of liquids <sup>[7]</sup>. The free space and its dependent properties have close connection with the molecular structure and it may show interesting features about interactions <sup>[8, 9]</sup>. This molecular interactions between like and unlike molecules are influenced by structural arrangement along with shape and size of the molecules. In the present study L.Arginine methyl ester dihydrochloride is taken as a solute and non-aqueous solution is the solvent. L-Arginine methyl ester dihydrochloride

enhances the body's ability to fight off diseases by improving the function of the immune system.

# II. EXPERIMENTAL TECHNIQUE

Solutions of the sample of different concentrations are prepared with AR grade salt. It is used without further purification. The solution is studied at different concentrations (0.001, 0.01, 0.05, 0.1, 0.2) mol. d.m<sup>-3</sup> with an accuracy of 0.0001gm is maintained. The density of the solutions is determined using 25ml specific gravity bottle, using the thermostatic bath with a compressor unit. A Cannon Fenske viscometer (10ml) was used for the viscosity measurements. Variable bath interferometer having a frequency of 2MHz (Mittal Enterprises, New Delhi) with overall accuracy of 0.1% was used for velocity measurements.

The FTIR spectrum of this solution is recorded in the region of 4000-400 cm<sup>-1</sup> using (PERKIN ELMER) model SPECTRUM RXI FTIR spectrometer.

The following formulae are used for the computation of Internal Pressure ( $\pi_i$ ), Free Volume (V<sub>f</sub>), Rao's constant and Wada's constant, Adiabatic compressibility:

- (i) Internal pressure  $\pi_{i} = bRT(k\eta/u)^{1/2} * \rho^{T}(2/3)/IM_{eff}T(7/6))atms$ .
- (ii) Free volume  $V_f = [M_{eff} * u/kŋ]^{3/2} cc;$

(iii)Rao's constant

$$R = \frac{M_{eff}(U)^{\frac{1}{3}}}{\rho}$$

(iv)Wada's constant

$$W = \frac{M_{eff}}{(\rho)\beta^{-1/\gamma}}$$

(v) Adiabatic compressibility

$$\beta = \left[\frac{1}{u^2 \rho}\right] cm^2 / dyne$$

Where

- K Constant equal to  $4.28 \times 10^9$
- $\eta$  Viscosity of the solution in poise
- u-ultrasonic velocity in cm/sec
- $\rho$  density of the solution in gm/cc
- b cubic constant(2)
- $R gas constant (8.324 x 10^7)$
- T temperature

 $M_{eff}$  - Effective molecular weight of the solution in gm

# III. RESULTS AND DISCUSSIONS

# A. Acoustic and Thermodynamic Study

1) Internal Pressure and Free Volume:

Internal pressure is a measurement of changes in energy of a system, when it expands or contracts at constant temperature. It has the same dimension as pressure. The significance of the internal pressure and its correlation with the solubility parameter is used in pharmaceutics, polymers and petroleum industry. Internal pressure arising out of the attraction forces of the molecules can be called the cohesive pressure and is dimensionally equivalent to the cohesive energy density.

Internal pressure can be expressed as sum of an attractive and repulsive contribution. The attractive forces mainly comprise hydrogen bonding, dipole-dipole, multipolar, and dispersion interactions. Repulsive forces, acting over very small intermolecular distances, play a minor role in the cohesion process under normal conditions. The concept of free volume is an extension of the idea that each molecule is enclosed by its neighbours in a cell, the free volume is however not the whole cell volume but rather than average volume in which the center of the molecule can move inside the hypothetical cell due to the repulsion of the surrounding molecules.

Internal pressure is a single factor which varies due to all the internal interactions <sup>[10]</sup>. In L-Arginine methyl ester dihydrochloride, the variations of internal pressure and free volume with temperature and molalities are shown in Figs. 1 and 2 and the values are tabulated in Table 1.

TABLE I VALUES OF INTERNAL PRESSURE  $(\Pi_1)$ , FREE VOLUME  $(V_F)$ , AND ADIABATIC COMPRESSIBILITY (B)

OF L-ARGININE METHYL ESTER DIHYDROCHOLORIDE IN NON-AQUEOUS SOLUTION

$\pi_i$ (atms)										
Temperature										
Molality (m)	278.	.15K	288.15K	298.15K	308.15K	318.15K	328.15K			
0.001	184	27.4	15984.3	13939.1	12203.2	10701.8	9904.0			
0.01	19236.4		16424.2	14136.2	12452.6	11100.8	10034.9			
0.05	19186.7		16871.5	14215.1	12501.9	11130.1	10037.0			
0.1	195	05.7	17248.5	14305.3	12646.1	11322.3	10036.7			
0.2	207	22.7	17602.3	14679.2	12907.5	11447.6	10217.2			
V <sub>f</sub> (cc)										
0.001	0.0097	796381	0.0164895	0.027256	0.0443671	0.0713996	0.097677334			
0.01	0.008602353		0.0151643	0.026049	0.0414926	0.0637588	0.093150965			
0.05	0.0085	533554	0.0137998	0.025269	0.0405385	0.0623417	0.091901057			
0.1	0.007970689		0.0127434	0.024385	0.0384437	0.0581758	0.090249101			
0.2	0.00643601		0.0115765	0.021826	0.0348244	0.0546868	0.082903379			
β (cm²/dyne)										
0.001	3.32	3.33	3.55		3.50	3.62	3.77			
0.01	3.33	3.30	3.47		3.58	3.63	3.74			
0.05	3.31	3.31	3.55		3.50	3.54	3.77			
0.1	3.34	3.33	3.53		3.53	3.60	3.70			
0.2	3.27	3.30	3.57		3.57	3.51	3.71			

In the sample internal pressure is found to be increasing with respect to increasing molality. But at 278.15K and (0.05m) it is observed as minimum. This decrease in internal pressure shows that there is a weak solute-solvent interaction prevails in the solution. It is also confirmed by increasing values of free volume at low molalities and at low temperature. Internal pressure decreases with increasing temperature for all molalities <sup>[11, 12]</sup>. But when the temperature is increased there is a tendency for the ions to move away from each other <sup>[13]</sup>. Hence there is a reduction in internal pressure with increase in temperature.



Fig. 1 Variations of internal  $pressure(\pi_i)$  and free volume (V<sub>f</sub>) with molality of L-Arginine methyl ester dihydrochloride in non-aqueous solutions at 278.15K - 328.15K



Fig.2 Variations of Rao's and Wada's constants with molality of L-Arginine methyl ester dihydrochloride in non-aqueous solutions at 278.15K - 328.15K

# 2) Adiabatic Compressibility:

The structural changes of molecules in the solution take place due to the existence of electrostatic field between the interacting molecules. The arrangement of molecules results in effect of adiabatic compressibility. the Adiabetic compressibility is an indication of the change in volume that results from a change in pressure when no heat flows in or out. When an electrolyte is dissolved in solvent, due to the influence of electrostatic field of the ions in the surrounding solvent molecules, the compressibility gets lowered. The lowering is attributed to the influence of the electrostatic field of the ions on the surrounding solvent molecules and the total internal pressure increases and solution becomes harder to compress.

The rise and fall is observed in adiabatic compressibility of the sample. It is shown in Fig. 3 and the values are tabulated in Table 1. These variations support a strong dissociation taking place between the molecules of the solution <sup>[14, 15]</sup>.



Fig. 3 Variations of adiabatic compressibility ( $\beta$ ) with molality of L-Arginine methyl ester dihydrochloride in non-aqueous solutions at 278.15K - 328.15K

When the temperature increases the associated groups of molecules break down increasingly and the forces of attraction between the molecules decreases <sup>[16]</sup>. This leads to an increase in the adiabatic compressibility of the system.

# 3) Rao's and Wada's Constants:

Method of studying the molecular interactions is to evaluate certain parameters, which are constants in noninteracting systems. The variation of these constants indicates the measure of interaction in interacting systems.

In L-Arginine Methyl Ester Dihydrochloride Rao's and Wada's constants are shown in the Figs. 4 and 5 and the values are tabulated in Table 2.



Fig. 4 Variations of Rao's constant with molality of L-Arginine methyl ester dihydrochloride in non-aqueous solutions at 278.15K - 328.15K



Fig. 5 Variations of Wada's with molality of L-Arginine methyl ester dihydrochloride in non-aqueous solutions at 278.15K - 328.15K

TABLE II VALUES OF RAO'S CONSTANT OR WADA'S CONSTANT

OF L-ARGININE METHYL ESTER DIHYDROCHOLORIDE IN NON-AQUEOUS SOLUTION

#### R (Rao's Constant)

Molality (M)	Temperature(K)								
	278.15	288.15	298.15	308.15	318.15	328.15			
0.001	2147.40	2162.08	2151.97	2170.88	2175.94	2177.75			
0.01	2147.67	2167.27	2163.55	2169.48	2178.68	2189.36			
0.05	2166.48	2178.59	2169.28	2189.25	2202.98	2199.72			
0.1	2182.39	2191.36	2189.25	2206.07	2217.06	2226.55			
0.2	2224.31	2232.01	2220.53	2243.07	2254.92	2257.95			

#### W (Wada's Constant)

0.001	1236.42	1243.66	1238.68	1248.00	1250.49	1251.38
0.01	1236.90	1246.57	1244.73	1247.66	1252.19	1257.45
0.05	1247.70	1253.68	1249.08	1258.94	1265.70	1264.09
0.1	1257.45	1261.88	1260.84	1269.13	1274.55	1279.23
0.2	1281.90	1285.70	1280.04	1291.16	1297.01	1298.50

In the sample, Rao's and Wada's constants are increasing with increasing concentration and temperature. These results lead to a curvilinear variation which indicates the weak structure of the solvent <sup>[17]</sup>. This behavior suggests that there is dissociation occurs in the solution.

# B. Fourier Transformer Infrared Spectral Analysis

The Infrared region  $(4000 - 650 \text{ cm}^{-1})$  is of great importance. It gives sufficient information about the structure of a compound. The technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic

compound. The absorption of infrared radiations (quantized) caused the various bands in a molecule to stretch in band width with respect to one another. Thus infrared spectra may be regarded as the finger print of a molecule.

The various stretching and bending vibrations of a bond occur at certain quantized frequencies. When infrared radiation is passed through the substance, energy is absorbed and the amplitude of the vibration is increased. From the excited state the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. As a result the temperature of the sample increases. The IR spectrum of absorption bands of specific functional groups, yet subtle interaction with the surrounding atom of the molecule imposes the stamp of individuality on the spectrum of every compound. FTIR is a powerful tool for identifying the elements present in the solution. In the present work L-Arginine methyl ester dihydrochloride solutions are analyzed by FTIR spectroscopic technique. The observed FTIR spectra of solvent and solute+solvent are shown in Figs. 6 and 7



Fig. 6 FTIR Spectrum of solvent

TABLE III SIGNATURE PEAKS OF SOLVENT AND L-ARGININE METHYL ESTER DIHYDROCHLORIDE SOLUTION

Name of the Sample/ Wavenumber cm <sup>-1</sup>	V <sub>NH</sub>	v <sub>CH</sub>	<b>v</b> <sub>C-N</sub>	v <sub>C=N</sub>	v <sub>C=0</sub>	δc =N	v <sub>C-0</sub>	$\delta_{\rm CH}$
Solvent	3416.24	2887.69	2772.25	1697.00	1550 (sh)	1389.74 1308.86	1054.09	602.52
Solvent + L.Arginine methyl ester dihydrochloride	3192.96	2885.82	2775.43	1690.41	-	1385.12 1306.32	1063.04	601.39



Fig. 7 FTIR Spectrum of solvent + solute



Fig. 8 Mirror image form of L-Arginine methyl ester dihydrochloride at chiral centers

L.Arginine methyl ester dihydrochloride is solvated by the solvent, there is a spectral decrease of the  $\delta NH_2$  stretching vibration by 224 cm<sup>-1</sup> in found. The enolic form with C=N group does not show much shift as well as the CO group. The signature peak of the amino acid is not affected much. The 1580 cm<sup>-1</sup> peak corresponding to the  $\delta NH$  bending vibrations has merged along with the CO vibration. A shift of about 7 cm<sup>-1</sup> is observed for this peak. The preferred binding sight of the Arginine methyl ester dihydrochloride in solvent should therefore be the NH<sub>2</sub> group, resulting in the structure for the charge solvated molecule <sup>[18]</sup>. It exists in mirror image form at the chiral centers is shown in Fig. 8. The protonated methyl ester of Arginine which lacks an acidic proton and it cannot form Zwitterion.

# IV. CONCLUSION

The acoustic and thermodynamic studies suggest that the intermolecular hydrogen bonding exists in the amino acid moiety. L.Arginine methyl ester dihydrochloride exhibits in non-zwitterionic (charge solvated) form. The sample is present in di-ionic form in L-Arginine methyl ester dihydrochloride. Study of Rao's and Wada's constants indicates that there is dissociation occurs in the solution. From the spectral analysis solvation with solvent molecules occurs at both NH<sup>+</sup> site of guanidino group. The preferred binding sight of the L-arginine methyl ester dihydochloride in solvent should therefore be the NH<sub>2</sub> group, resulting in the structure for the charge solvated molecule.

The results obtained from Acoustic and Thermodynamic analysis are well correlated with spectroscopic study.

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